VOL. I. 1902

TRANSACTIONS

OF THE

AMERICAN ELECTROCHEMICAL SOCIETY.

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TRANSACTIONS

OF THE

AMERICAN ELECTROCHEMICAL SOCIETY.

VOLUME. 1.

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PHILADELPHIA INAUGURAL MEETING.
APRIL 3, 4, 5, 1902.

PUBLISHED BY
THE AMERICAN ELECTROCHEMICAL SOCIETY,
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TABLE OF CONTENTS.

PAGE

Portrait of President Joseph W. Richards ..... Frontispiece
The American Electrochemical Society. Introductory.—Richards 1
Historical Sketch 3
Proceedings 4
Constitution 13
Catalogues of Charter Members ..... 19 and 30

PAPERS.

A University Course in Electrochemistry.—Richards 41
Graphite Electrodes in Electrometallurgical Processes.—Collins 53
Note on the Gladstone-Tribe Couple.—Bancroft 65
The Nascent State.—Reed 69
The Electrical Reduction of Lead.—Salom 87
Electrolytic Refining of Composite Metals.—Ulke 95
A Novel Concentration Cell.—Carhart 105
The Manufacture of Bisulphide of Carbon in the Electric Furnace.—Taylor 115
Current Electrochemical Theories.—Kahlenberg 119
A Zinc-Bromide Storage Battery.—Dow 127
Continuous Electrolysis of Solutions of Metals.—Keith 131
A Method of Electrolytic Production of Zinc from its Ores.—Sadtler ... 141
The Electrolytic Rectifier.—Burgess and Hambuechen 147
Caustic Alkalies and Chlorine by the Dry Electrolytic Process.—Acker. 165
On the Relative Velocities of the Ions in Solutions of Silver Nitrate in Pyridine and Acetonitrile.—Schlundt 177
On a New Type of Electrolytic Meter.—Norden 181
The Reversible Copper Oxide Plate.—Johnson 187
A Thermodynamical Note on the Theory of the Edison Accumulator.—Roeber 195
Electrolysis by an Alternating Current.—Richards 221
The Atom of Electrochemistry.—Reuterdahl 229
Obituary Notice of Charles T. Child 246
Index of Subjects and Authors 247

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VOLUME I. NO. I.

TRANSACTIONS

OF THE

AMERICAN ELECTROCHEMICAL SOCIETY

THE AMERICAN ELECTROCHEMICAL SOCIETY.

Division of labor in industry has its analogue in specialization in science. To do one thing and do it well is the key-note of perfection in the mechanic arts, and likewise the watchword of progress in the realm of observation and research.

The man who is jack of all trades, is proverbially the master of none ; the scientist who dabbles in several fields quickly earns the reproach of a superficialist, and seldom makes real progress in any ; the society which has all the world for its field, is usually on a par with them both.

Differentiation and specialization are the watchword, now, of all progress,—industrial, scientific, philosophical. The day is past, we all acknowledge, when one man, even be he Newton, can know all that is to be known ; the day is also past when one scientific society can cover satisfactorily the whole field of scientific research. Even more than this, the day is passing when any one society can even cover satisfactorily the whole field of any one science, such as physics or chemistry or medicine.

Evidence accumulates on every hand that the analogue of the specialist in science is the *society which specializes*. Whether for good or ill, whether some of its influences are narrowing in some directions or not, the society which specializes is the necessary corollary of the scientific specialist ; the latter came perforce into existence, has made the whole world his debtor, and is recog-

nized as the present factor for progress; the former is coming perforce into existence, will soon make the world its immeasurable debtor, and will be a wonderfully potent factor in future scientific progress.

Such is the force, the necessary condition, which has brought into existence The American Electrochemical Society. It could not help but come into existence; the development of the electrochemical industries and the large increase in the number of electrochemical specialists, has made its formation imperative. Its functions should be those of bringing electrochemists into personal contact with each other; of disseminating among them all the information known to, and which can be spared by, their co-workers; to stimulate original thought in these lines by mutual interchange of experience, and by papers and discussions; to stimulate electrochemical work all over the world by publishing the news of what is being done here in America. No one interested in electrochemistry can belong to such a society and participate in its work, without receiving from it many times more than the small share he contributes.

Such a society in America being, therefore, a necessity, a pressing need, its formation was inevitable. It came. The forces at work crystallized in Philadelphia, in the fall of 1901, and as the result of a general call for a meeting, 353 members gave in their names and 20 papers were read and discussed at *the meeting for organization*. The results have justified the insight of the projectors of the society, the first meeting has been an enthusiastic success, the organization now exists, its future is one of assured usefulness. With confidence we stand out to sea.

RICHARDS.

HISTORICAL SKETCH.

The preliminary meeting which resulted in the formation of the American Electrochemical Society, was called by the following circular, sent to about thirty residents of the United States supposed to be especially interested in electrochemistry:

PHILADELPHIA, Oct. 19, 1901.

DEAR SIR:—

The rapidly growing importance of the subject of electrochemistry, and the want of suitable occasions in this country for the discussion of papers and questions pertaining thereto by those specially interested, have suggested the advisability of founding a National Electrochemical Society, similar in its organization to the American Chemical Society and the American Institute of Electrical Engineers.

You are invited, as one of about a dozen or twenty who are believed to be specially interested in this subject, to attend a preliminary meeting to be held at the Engineers' Club, 1122 Girard St. (near 12th and Chestnut Sts.), Philadelphia, on Friday, Nov. 1, 1901, 8 P.M., at which it is proposed to discuss the general plans for the organization of such a society and to appoint various committees which are to arrange for a formal meeting to be held as soon as practicable, at which the society is to be founded, a constitution adopted, and papers read and discussed.

Should you be unable to attend the preliminary meeting, a letter stating your opinions concerning the question of the advisability of founding such a society, and the general plans of its organization, would be appreciated and will be read at the meeting.

Please address your reply to any one of the undersigned.

Yours respectfully,

CARL HERING,
929 Chestnut St., Philadelphia.

C. J. REED,
3313 N. 16th St., Philadelphia.

PROF. JOSEPH W. RICHARDS, PH.D.,
Lehigh University, Bethlehem, Pa.

E. F. ROEBER, PH.D.,
929 Chestnut St., Philadelphia.

PROF. SAMUEL P. SADTLER, PH.D.,
N. E. Cor. 10th and Chestnut Sts.,
Philadelphia.

DR. WM. H. WAHL, PH.D.,
Franklin Institute, Philadelphia.

PROPOSED AMERICAN ELECTROCHEMICAL SOCIETY.

MINUTES OF PRELIMINARY MEETING, NOVEMBER 1, 1901.

The meeting was held at the rooms of the Engineers' Club, 1122 Girard Street, Philadelphia, on November 1, 1901, in response to a circular letter of invitation signed by Messrs. Hering, Reed, Richards, Roeber, Sadtler, and Wahl, a copy of which is appended to these minutes.[1] This letter which was sent to about thirty engineers, chemists, and scientists, who were thought to be especially interested in the subject of electrochemistry, suggested the founding of a National Electrochemical Society, and invited those addressed to meet to discuss the advisability of its formation, the general plans for organizing it, and the arrangements for holding a formal meeting for founding it.

The meeting began at 8.15 P.M. There were present :

W. D. Bancroft, Ph.D., Professor of Physical Chemistry at Cornell University, Ithaca, N. Y.; J. D. Darling, Chemist of Harrison Bros. Co., Phila., Pa.; C. A. Doremus, M.D., Ph.D., Professor of Chemistry, College of the City of New York, Past Vice-President American Chemical Society, New York City; Carl Hering, Consulting Electrical Engineer, Past President American Institute Electrical Engineers, Phila.; Louis A. Parsons, Johns Hopkins University, Baltimore, Md.; C. J. Reed, Electrochemical Engineer, Phila.; J. W. Richards, Ph.D., Assistant Professor of Metallurgy at Lehigh University, Bethlehem, Pa., Vice-President of American Chemical Society ; E. F. Roeber, Ph.D., Electrical Engineer, Phila.; S. P. Sadtler, Ph.D., Consulting Chemist, formerly Professor at the University of Pennsylvania, Phila., Pa.; William H. Wahl, Ph.D., Secretary Franklin Institute, Philadelphia ; G. M. Westman, Metallurgist, New York.

Professor J. W. Richards, of Bethlehem, was elected Chairman and Carl Hering secretary. Letters were then read from those who could not be present, most of which were favorable to the founding of such a society. Some were neutral and a few unfavorable. These letters are duly filed.

The question of the advisability of forming such a society was then discussed, the concensus of opinion being decidedly favorable.

[1] See above.

Mr. Reed moved that it be founded at the present meeting ; the motion was lost.

Mr. Reed moved that the chair appoint a Membership Committee of five to solicit members and to ascertain the number of members that could be secured. Carried.

Mr. Hering moved that a committee of three be appointed to arrange for a meeting for organization, and to secure papers, when the Membership Committee reports favorably concerning the number of members. Carried.

Dr. Wahl moved that the promise of at least 100 prospective members should be secured by the Membership Committee, before the arrangements for an organization meeting should be made. Mr. Reed moved to amend this to 50 ; the amendment was lost. Mr. Hering moved to amend it to 75. The motion was carried.

On motion of Mr. Reed the Membership Committee was instructed to say to prospective members that the annual dues should not exceed $5.00.

On motion of Mr. Hering the Membership Committee was furthermore instructed to say that the intention was to hold only a few meetings each year and that these were to be held in different cities.

Mr. Hering moved that the name of the prospective society shall be the American Electrochemical Society. Carried.

Mr. Hering moved that a committee of five be appointed by the Chair to prepare a proposed Constitution and By-Laws for the society, based on those of the American Institute of Electrical Engineers, and of the American Chemical Society, provided the Membership Committee has secured the required number of names. Carried.

The meeting then adjourned at 10.30 P.M. to meet at the call of the Chair.

CARL HERING, *Secretary*.

The committees appointed are as follows :

Committee on Membership.—Messrs. Doremus (Chairman), Bancroft, Reed, Richards, Roeber.

Committee on Meetings and Papers.—Messrs. S. P. Sadtler (Chairman), Roeber, Salom.

Committee on Constitution and By-Laws.—Messrs. Hering (Chairman), Bancroft, Doremus, Richards, Wahl.

Committee on Finance (appointed subsequently to raise funds for the organization meeting).—Messrs. Wahl (Chairman), Darling, Salom.

Pursuant to instructions of the Preliminary Meeting of Nov. 1, 1901, the Committee on Membership sent out the following circular letter to all members of the American Chemical Society, and to all members of the American Institute of Electrical Engineers, and also to such other persons,—engineers, chemists and metallurgists as were known to the committee to be interested in the development of electrochemistry:

NEW YORK, November 25, 1901.

DEAR SIR:—

The products of electrochemical industries in this country at the present time amount to about $100,000,000 per year. The growing importance of these industries and the fact that scientists and engineers interested in electrochemistry are now distributed among at least half a dozen different societies, and, therefore, have no common medium of communication, suggested the formation of an American Electrochemical Society on the same general plan as the American Chemical Society and the American Institute of Electrical Engineers.

A preliminary meeting in the interest of such an organization was held November 1, 1901, at the Engineers' Club, of Philadelphia, Prof. J. W. Richards, Vice-President of the American Chemical Society, acting as Chairman, and Mr. Carl Hering, Past-President of the American Institute of Electrical Engineers, as Secretary. All of those present were heartily in favor of forming such a society and numerous encouraging letters were received from all parts of the country, those from representatives of the electrochemical industries being especially favorable. It was unanimously decided that such a society should be founded as soon as a sufficient number of members could be obtained to insure success. Committees were appointed to secure members and to arrange for a meeting in the near future, at which the society should be formally organized. It was the opinion of those present at the preliminary meeting that the annual dues should not exceed $5 and that there should be only one class of members.

The bringing together in this way of those engaged in the scientific study of electrochemistry, and the practical engineers and pioneers of the industry, will be of inestimable value to both.

The undersigned Committee of Membership earnestly solicits your coöperation and asks you to notify the chairman, Dr. Charles A. Doremus, 17 Lexington Avenue, New York, before December 31st, that you can be depended upon to become a charter member.

Yours very truly,

CHARLES A. DOREMUS, *Chairman*,
W. D. BANCROFT,
J. W. RICHARDS,
E. F. ROEBER,
C. J. REED.

AMERICAN ELECTROCHEMICAL SOCIETY.

MINUTES OF THE ORGANIZATION MEETING, HELD AT THE MANUFACTURERS' CLUB, PHILADELPHIA, PA., THURSDAY, APRIL 3, 1902, J. W. RICHARDS, CHAIRMAN, CARL HERING, SECRETARY.

The meeting was called to order at 8.30 P.M. There were present 52 persons. The minutes of the preliminary meeting of November 1, 1901, were read and approved. Brief reports were made by the following committees: Committee on Membership, Committee on Papers and Meetings, Committee on Constitution and By-Laws, Committee on Finance.

N. S. Keith moved that "We now proceed to organize the American Electrochemical Society." Carried unanimously.

C. J. Reed moved that the name of the society be "The American Electrochemical Society." An amendment by Carl Hering to write the word electrochemical with a hyphen and a Capital C was lost by a vote of 21 to 29, and the original motion was then carried.

C. J. Reed moved that the following officers be elected: a president, for a term of one year; six vice-presidents, three to serve one year and the other three, two years; nine managers, divided into three classes, three to go out in one year, three to go out in two years, and three to go out in three years; and a secretary and a treasurer, each for one year. This list of officers and their terms of office is in accordance with the proposed constitution. The motion was carried with the amendment that the terms of office should be decided by lot.

On motion of Col. Reber the Chairman appointed a Nominating Committee of five to prepare a ticket to be presented to the Society. The Chair appointed Messrs. Reed, Roeber, Lloyd, Fraley, and Weaver to constitute this committee.

A motion to appoint two Nominating Committees of five each, so as to have two tickets, and to increase the committee to seven, so as to include the temporary chairman and secretary, was lost.

On motion of Mr. Coho, the acting Chairman, Professor J. W.

Richards, Ph.D., of Lehigh University, Bethlehem, Pa., was elected President unanimously.

Mr. Hering moved that Mr. C. J. Reed, the prime mover in the organization of this Society, be elected Secretary, but as the nominations were to be left to the committee the motion was withdrawn.

A recess was then taken during which several communications were read by the Secretary, including an invitation to the Society from the Citizens' Business League, of Milwaukee, to hold their next convention in that city. (Applause.)

After the recess the Nominating Committee reported as follows: For Vice-Presidents : C. A. Doremus, of New York; H. S. Carhart, of Ann Arbor, Michigan ; C. M. Hall, of Niagara Falls ; W. D. Bancroft, of Ithaca, N. Y.; L. Kahlenberg, of Madison, Wis.; W. R. Whitney, of Boston, Mass.; alternates, E. G. Acheson, C. S. Jacobs, and E. C. Acker. For Managers : Carl Hering, of Philadelphia ; E. G. Acheson, of Niagara Falls ; E. F. Roeber, of Philadelphia ; S. P. Sadtler, of Philadelphia ; C. O. Mailloux, of New York; Edw. Weston, of Waverly Park, N. J.; Samuel Sheldon, of Brooklyn ; W. D. Weaver, of New York ; Samuel Reber, of Washington, D. C.; alternates, T. Wolcott, C. P. Townsend, H. Rodman, J. L. R. Morgan, E. R. Taylor, and M. C. Lloyd. For Treasurer : Pedro G. Salom, of Philadelphia. For Secretary : C. J. Reed, of Philadelphia.

On motion of Carl Hering those nominated by the committee, with the exception of the alternates, were unanimously elected.

The temporary secretary was then relieved by the newly elected secretary.

CARL HERING,
Temporary Secretary.

The Committee on Constitution and By-Laws, appointed at the meeting of November 1, 1901, then reported a proposed Constitution, which, after some discussion, was referred to the Board of Directors for final adoption as to phraseology, with instructions to incorporate in the Constitution the principles outlined in the report of the committee, and also the following articles :

"That the name of the Society be The American Electrochemical Society."

"That it shall be the duty of the president to call a special meeting at the written request of 30 members."

"That a majority of the Executive Committee shall constitute a quorum."

On motion it was decided to determine by lot, at once, which of the vice-presidents already elected should serve for one and which for two years; also which of the managers already elected should serve for one, which for two, and which for three years. The president appointed as tellers to make the drawing Mr. Mullin and Mr. Hunter, who reported as follows:

Vice-Presidents: For two years, Hall, Kahlenberg, Carhart; for one year, Bancroft, Doremus, Whitney.

Managers: For three years, Hering, Weaver, Roeber; for two years, Acheson, Weston, Sheldon; for one year, Reber, Sadtler, Mailloux.

On motion of Mr. Hering it was decided that the question of publications should be referred to a committee to be appointed by the Board of Directors, with power to act.

On motion of Mr. Hering it was decided that the question of publishing the papers presented to the Society should be left to the Board of Directors.

On motion of Mr. Hering the thanks of the Society were voted to the Manufacturers' Club for the courtesies they had extended to the Society.

On motion the thanks of the Society were voted to the gentlemen who gave their time and energy to establishing this Electrochemical Society.

On motion the expenses already incurred were referred to the Board of Directors with power to act thereon.

Mr. Hering announced that the University of Pennsylvania had invited the Society to luncheon to-morrow afternoon.

The president called a meeting of the Board of Directors for Friday evening, at 8 o'clock.

The meeting then adjourned to meet Friday morning at the University of Pennsylvania, at the John Harrison Chemical Laboratory.

C. J. Reed,
Secretary.

REPORT OF MEMBERSHIP COMMITTEE.

PHILADELPHIA, PA., April 3, 1902.

Dr. Joseph W. Richards, Chairman, and others, of Preliminary Meeting of Proposed American Electrochemical Society.

GENTLEMEN:—

The Committee on Membership begs leave to report that in response to the invitations sent out by your Committee to members of the American Chemical Society and members of the American Institute of Electrical Engineers and to such other electricians, engineers, and chemists as were known to your Committee to be interested in electrochemistry, favorable replies have been received from 337 persons, one only having subsequently withdrawn. These responses are from 36 states of the United States and 8 foreign countries. The foreign countries are Australia, Canada, England, France, Hawaii, Italy, Mexico, and Switzerland.

The states having the largest representations are: New York, 112; Pennsylvania, 56; Massachusetts, 26; New Jersey, 18; Illinois, 10; California, 9; Wisconsin, 9; Ohio, 8; foreign, 24; total, 272.

This leaves 65 members distributed among the remaining 28 states.

The sentiment expressed in about 90 per cent. of the replies received, was that a society like the one proposed is now an imperative necessity, and that through its instrumentality inestimable benefits will accrue to both applied and theoretical electrochemistry.

CHARLES A. DOREMUS, *Chairman*,
WILDER D. BANCROFT,
JOSEPH W. RICHARDS,
CHARLES J. REED,
E. F. ROEBER.

REPORT OF THE COMMITTEE ON PAPERS AND MEETINGS.

READ APRIL 3, 1902.

The work done by the committee is embodied in the printed program.

Three additional papers have been announced: Titus Ulke, Sault Ste. Marie, Ontario, Canada. "The Electrolytic Refining of Composite Metals."

Edward R. Taylor, Penn Yan, N. Y. "Manufacture of Bisulphide of Carbon in the Electric Furnace."

Professor Henry S. Carhart, University of Michigan, Ann Arbor, Mich. "A Novel Concentration Cell."

Details have been arranged, including a stenographer to take down the discussion.

The University of Pennsylvania has extended to the Society a cordial invitation to luncheon on Friday, between the two sessions.

SAMUEL P. SADTLER,
P. G. SALOM,
E. F. ROEBER.

PHILADELPHIA, April 3, 1902.

BOARD OF DIRECTORS' MEETING, APRIL 4, 1902.

A meeting of the Board of Directors was held at the Manufacturers' Club, 1409 Walnut St., at 8 P.M., at which the following members of the Executive Committee were appointed: P. G. Salom, Carl Hering, Dr. E. F. Roeber, C. J. Reed, Dr. Chas. A. Doremus, Dr. J. W. Richards.

C. J. REED,
Secretary.

EXECUTIVE COMMITTEE MEETING, APRIL 4, 1902.

A meeting of the Executive Committee of the American Electrochemical Society was held at the Manufacturers' Club, at 8.30 P.M., April 4, 1902. The following members were present: Salom, Hering, Roeber, Reed, Richards; also the following directors: Weaver, Carhart.

The following Committee on Publication was appointed: Salom, Hering, Weaver, Richards.

The Committee on Publication was instructed to obtain bids for the publishing of 1,000 copies of the transactions of the inaugural meeting.

An invitation was received to hold the next general meeting of the Society at Niagara Falls, in September, 1902, and was accepted.

It was decided to deposit the funds of the Society in the Fourth Street National Bank of Philadelphia in the name of the American Electrochemical Society.

The secretary was instructed to procure all necessary stationery with the addresses of the president, secretary, and treasurer.

Bills were approved to the amount of $156.65.

C. J. REED,
Secretary.

CONSTITUTION

OF THE

AMERICAN ELECTROCHEMICAL SOCIETY.

Article I.

Name and Objects.

1. The name of this association shall be the American Electrochemical Society.

2. Its objects shall be the advancement of the theory and practice of Electrochemistry. Among the means to this end shall be the holding of meetings for the reading and discussion of professional and scientific papers on this subject, the publication of such papers, discussions and communications as may seem expedient, and coöperation with chemical, electrical and other scientific and technical societies.

Article II.

Membership.

1. There shall be only one class of members.

2. The only requirement for eligibility to nomination as member is that the candidate shall be interested in the subject of electrochemistry.

Article III.

Admission and Dismissal of Members.

1. Those who have, prior to April 6, 1902, notified the proper authorities that they wish to become members of the Society, are by the adoption of this constitution elected as charter members. They shall not be required to pay an entrance fee; they shall, however, be required to pay their dues for the current year within three months.

2. Application for admission after April 6, 1902, shall be made in writing in a form prescribed by the Board of Directors, and shall refer to at least two members. If the applicant is unable to do this he shall refer to at least three persons, including their addresses, of reputable standing, preferably electrochemists,

chemists, electrical engineers, professors or instructors in institutions of learning. The application shall also state the present occupation of the applicant, and briefly in what capacity he is interested in the subject of electrochemistry.

3. The secretary shall send to each director at least twenty days before an election, the names and addresses of the applicants and of their respective references, provided the applications are in due form. The Board of Directors at a duly called meeting shall consider such applications. The election to membership shall be by a vote of the Board of Directors at that or at a subsequent meeting. Proxy votes shall be included; also mail votes received before the election. Two negative votes shall exclude a candidate. The Board of Directors may refuse to elect a candidate whose character, reputation, or professional conduct would make him, in the opinion of the Board of Directors, an undesirable member. The names of those only who have been elected, shall be announced to the Society. A candidate who has been duly elected shall be placed on the rolls and have all the rights and privileges of a member as soon as his entrance fee and dues for the current year have been paid.

4. A member desiring to resign shall send a written communication to the Secretary, who shall accept and announce the resignation provided the dues and other indebtedness of that member have been paid to the mailing of his resignation.

5. Upon the written request of ten or more members that, for cause stated therein, a member be dismissed, the Board of Directors shall consider the matter, and if there appears to be sufficient reason, shall advise the accused of the charges against him. He shall then have the right to present a written deference, and to appear in person before a meeting of the Board of Directors, of which meeting he shall receive notice at least twenty days in advance. Not less than two months after such meeting, the Board of Directors shall finally consider the case, and if in the opinion of the majority of the Board of Directors a satisfactory defense has not been made, and the accused member has not in the meantime tendered his resignation, he shall be dismissed from the Society.

Article IV.

Dues.

1. The entrance fee, payable on notification of election, shall

be five dollars. (Charter members shall be exempt from the payment of the entrance fee.) If not paid within three months after notification, the election of the applicant is thereby canceled.

2. The annual dues shall be five dollars. They shall be due at the beginning of the calendar year, and notice thereof shall be mailed to each member before the end of the preceding year. If not paid before the annual meeting, the delinquent member shall lose his right to vote or to receive the publications of the Society, until said dues are paid. Members will pay dues for, and receive the publications of, the year in which they are elected, but if elected within two months of the end of the calendar year may, at their option, pay for, and enter with, the next coming year.

3. Any member who, at an annual meeting, is in arrears for two years shall be dropped from the rolls, and shall not be included in subsequently published lists of members. The Board of Directors may reinstate a member who has been dropped, provided all his arrears have been paid.

Article V.

Officers.

1. The officers of the Society shall be a President, six Vice-Presidents, nine Managers, a Secretary, and a Treasurer, who shall hold office as follows:

2. The President, the Secretary, and the Treasurer for one year, the Vice-Presidents for two years, and the Managers for three years. At each annual meeting a President, three Vice-Presidents, three Managers, a Secretary, and a Treasurer shall be elected and their term of office shall begin at the close of the annual meeting, except during the year 1902, when it shall begin with their election. Each officer shall hold office until his successor has qualified.

3. A vacancy in the office of President shall be filled by the senior Vice-President; a vacancy in the office of Vice-President shall be filled by the senior Manager. Seniority between officers of the same rank and date of election shall be determined by the number of votes received when they were elected; or if the same, then by the date of their election to membership, or if this be also the same, then in alphabetical order. All other vacancies shall be filled by the Board of Directors.

4. No officer shall receive directly or indirectly, any salary,

compensation or emolument from the Society, either as such officer or in any other capacity, or be interested, directly or indirectly, in any contract relative to the operations conducted by the Society or in any contract for furnishing supplies thereto, unless authorized either by the by-laws or by a vote of the majority of the entire Board of Directors.

Article VI.

Election of Officers.

Nominations for officers will be received by the secretary not later than the first of February. He shall mail a printed list of these with the notice for the annual meeting to every member. The voting need not be restricted to the names on this list. The Board of Directors may endorse those which it prefers and if so, the published list shall state it. The voting shall be by secret letter ballot, the voter shall sign his name on the outside envelope and the ballot shall be enclosed in the inner sealed envelope. Ballots must reach the secretary not later than the evening of the first day of the annual meeting. The results of the election shall be announced at one of the sessions of that annual meeting. The Board of Directors shall appoint the tellers.

Article VII.

Management.

1. The affairs of the Society shall be managed by a Board of Directors under this constitution and by-laws. This board shall consist of the officers and the two junior past presidents. The President, Vice-President, Secretary, and Treasurer of the Society shall hold the same offices in this Board of Directors.

2. The Board of Directors shall prepare and adopt a series of by-laws which shall govern its meetings and its procedure, as also that of the Society under this constitution. It shall require a two-thirds vote of the whole board to adopt or amend these by-laws; proxy and mail votes shall be counted when received before the vote is counted. The text of the proposed by-laws or amendments shall be furnished to each member of the Board of Directors at least ten days before the meeting at which the vote on the same is to be taken.

3. The Board of Directors may delegate any or all of its powers, except in those cases in which this constitution requires a vote of

the whole board, to an Executive Committee of not less than one-third of the number of members of the Board of Directors. The President and Secretary shall be members of this Executive Committee. This committee shall conduct the affairs of the Board of Directors between its meetings. All members of the Board of Directors shall receive notice of the meetings of this Executive Committee and shall have the right to attend and vote. A majority of the Executive Committee shall constitute a quorum.

4. At the request of the President, matters requiring action by the Board of Directors may be discussed and voted upon by a mail vote of the Board of Directors.

5. The duties of the officers shall be such as usually pertain to the offices they hold, besides any others designated in the constitution or by-laws or by the Board of Directors. The Secretary shall, under the direction of the President and Board of Directors, be the executive officer of the Society. The Secretary and the Treasurer shall present reports annually to the Board of Directors, before the annual meeting. The Board of Directors shall present a report annually to the Society at its annual meeting. The nature of these reports shall be specified in the by-laws.

6. All standing committees shall be directly responsible to the Board of Directors, and shall be appointed by the President or by the Board of Directors.

Article VIII.

Meetings.

1. The annual meeting shall be held during or about March or April. Business affecting the organization of the Society shall be transacted only at the annual meetings. Proxy or mail votes shall be received.

2. Other meetings may be held at such times and places as the Board of Directors shall select. The President shall call a meeting at the written request of 30 or more members.

3. Notice of all ordinary meetings shall be sent to all members at least 20 days in advance, and of the annual meeting, 30 days in advance.

Article IX.

General.

1. A quorum of the Society shall consist of one-tenth the num-

ber of members residing in the United States, present in person or by proxy.

2. Every member entitled to vote at any meeting may vote by proxy or, when the subject-matter has not been changed, by mail. No proxy shall be valid after the expiration of eleven months from the date of its execution. Every proxy shall be revocable at the pleasure of the person executing it.

3. The fiscal year of the Society shall begin January 1st.

Article X.

Amendments.

Proposals to amend this constitution shall be made in writing to the Board of Directors and signed by at least ten members; they shall reach the Secretary not later than February 1st. The Board of Directors shall consider them and may amend them. The original, with the action of the Board of Directors, shall then be presented to the Society at its annual meeting, for final action. A majority vote shall decide, the proxies being included, provided that a quorum is represented, in person or by proxy.

AMERICAN ELECTROCHEMICAL SOCIETY.

CATALOGUE OF CHARTER MEMBERS.

April 3, 1902.

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A paper read at the Inaugural Meeting of the American Electrochemical Society, Philadelphia, April 4, 1902, Vice-President Doremus in the Chair.

A UNIVERSITY COURSE IN ELECTROCHEMISTRY.

By Joseph W. Richards.

A course in electrochemistry should be designed to cover the needs of that rapidly expanding field,—the applications of the electric current to the chemical and metallurgical arts. It must be designed to fill three requirements; *viz.*, it should be educative, in the sense of developing the power of observation, reasoning and the ability for research; it should also be practical in that it fits a student to earn his living by being at once able to make himself useful in an electrochemical establishment; by so doing, it will fill also the third requirement, that of supplying the electrochemical industries with the most suitable men for their needs. The importance and rapid development of this industrial field is one of the most marked industrial changes of recent years, and the demand for university-trained men particularly fitted to enter it is already pressing and will undoubtedly increase.

The applications of the electric current above referred to are, more specifically, the extraction of metals from their ores or compounds (aluminum, magnesium, sodium, zinc, nickel, antimony, tin, lead, copper, silver, gold); the refining of crude metals (zinc, nickel, copper, silver, gold); the electroplating of metals (gold, silver, platinum, nickel, brass, copper); the manufacture of metallic carbides and silicides (alkaline earth carbides and silicides, silicon carbide); the purification of impure ores (alumina); the manufacture of artificial abrasives (carborundum and emery); of artificial graphite or diamond; electromagnetic treatment of ores and minerals; preparation of caustic alkali and chlorine; preparation of chlorates and chlorites; caustic alkaline earths; phosphorus, ozone; nitric acid from atmospheric nitrogen; artificial pigments, both inorganic and organic; the rationale of batteries and storage cells; thermoelectric cells; electric furnaces for various uses; electric soldering and welding; electrolytic hydrogen and oxygen; electrolytic oxidations and reductions, in general, in industrial chemical operations.

The question now to be discussed is this: Given a bright young man with a collegiate or first-class high school education, in what manner can his studies be best directed, during four years of university undergraduate work, to fit him for the field above outlined? The field is large, and four years is the definite time available; the problem is to make a wise selection and correlation of such fundamental studies as the course should contain.

Heretofore, speaking of our American universities and technical schools in general, the student with a desire to learn electrochemistry and an ultimate view of entering that field, has had before him the choice of three lines of study, each approximating towards this end but none filling the conditions completely; *viz.*, the courses in chemistry, electricity, or metallurgy.

The course in chemistry concerns so many departments of chemical activity that but a very small part of it is devoted to the mutual relations and inter-reactions of electrical and chemical energy, and still less to what may be called electrical engineering. The graduate of this course has usually a very slight acquaintance with electrical subjects.

A course in metallurgy usually differs from the chemical course in going less into detail in unusual analyses, in containing very little organic chemistry, and in place of these taking up the elements of some mining, mechanical, or electrical engineering subjects, such as petrology, geology, dressing of ores, steam engines, mechanical technology, and electrical laboratory. The graduate of this course is well equipped in chemistry and has considerable engineering knowledge, but is no more an electrician than he is a mining or a mechanical engineer. He is, however, in my opinion, better equipped for electrochemical work than by the purely chemical course.

The course in electrical engineering is unsuited as a preparation for electrochemical work because of the very minor part necessarily assigned therein to metallurgy and chemistry studies, which must be begun early to be learned properly and well. It is less suited to the prospective electrochemist than the metallurgical course, because of this deficiency.

Assuming that the above is a fair statement of the present status of those three courses, the most satisfactory preparation for the would-be electrochemist has been to first complete the chemical or the metallurgical course and then to take electrical

engineering in addition,—a matter of at least six years' study, but a splendid combination if the student can devote that time. Even in this combination, however, some very desirable elements may be found wanting, such as thorough instruction in the interrelations of chemical and electrical energy and experimental laboratory work in an electrochemical laboratory. There is a certain borderland between the two sciences, electricity and chemistry, which requires a very thorough understanding of the fundamental principles of both sciences in order to be properly comprehended, and hence the exploring of this borderland is generally left out of both the chemical and the electrical curriculum, because it would not be easily understood by the student in either course. Study and work in this borderland require for their proper performance and appreciation a chemical and an electrical training such as those who take chemistry alone and electricity alone usually lack, and, therefore, such studies are usually not to be found in either course.

What then must be the object and methods of a course in electrochemistry designed to overcome these difficulties and fulfil these desiderata? It must contain thorough drill in the fundamental principles of both chemistry and electricity and a full treatment or covering of the borderland between the two sciences, which is the special province of electrochemistry as a pure science ; while grouped in and around these main outlines, must be a carefully selected variety of chemical, electrical, mechanical, and general science subjects, rounded out by the necessary culture studies common to all broad education.

This end is best attained, in the writer's opinion, by starting with the course in metallurgy and modifying it so as to include the fundamentals of electrical engineering and adding thereto lectures and laboratory work in specific electrochemical subjects, —the borderland studies. The metallurgical course already contains as much chemical study as it is possible to get into an electrochemical course of four years. The modifications of the metallurgical course would consist in omitting from it some of the studies having more direct connection with mining, mechanical, and civil engineering (such as geology, petrology, graphic statics of mechanisms, hydraulics) and replacing them by such electrical studies as are of primary importance to the electrochemist (such as further study of electricity and magnetism in general, the theory

and tests of direct and alternating current dynamos and motors, generating plants, transmitting, transforming, and receiving systems) and adding the borderland studies (such as theories of electrolysis, electrolytic laboratory work, etc.).

It is probable that the course thus constructed will not only be found to meet the practical needs of the student wishing to enter the electrochemical industries, but also that it will possess a high educative value. The nature of the studies included in it, the becoming familiar with the essential principles of two great fields of science, and especially the detailed study of subjects uniting the two sciences in intimate relations will, I believe, give to the student and resulting electrochemist a breadth of view and attainment not possible to any one who specializes in either field alone.

Admission to the course proposed would be gained by passing satisfactory examinations in English, German or French, American history and geography, elementary physics, algebra, geometry, and the plane trigonometry and logarithms. These examinations are to be such as would be within the ability of the graduate of a good high school.

The course itself would then include the following subjects:

Mathematics.—Advanced algebra, trigonometry, elementary mechanics, analytical geometry, differential and integral calculus.

Physics.—Mechanics and heat, electricity and magnetism, sound and light, all by lectures, recitations, problems and laboratory work.

Chemistry.—General lectures, experimental laboratory work, qualitative and quantitative analysis, stoichiometry, chemical philosophy, qualitative and quantitative blowpipe analysis.

Electrical Engineering.[1]—Advanced theory of electricity and magnetism (4), with laboratory (3); theory of direct current dynamos and motors (2), with laboratory work (3); theory of alternating currents (2), with laboratory work (3); electrical generating stations for light and power (2); electrical transmission and receiving systems.

Electrochemical.—Theories of electrolysis (1); electrolytic laboratory (1); electrometallurgical process (1); electric furnace laboratory (1).

Metallurgy.—General metallurgy and the metallurgy of iron

[1] The numbers show the exercises per week for one semester.

and steel (5); metallurgy of non-ferrous metals (4); metallurgical problems (1); metallurgical construction (3) and design (2); metallurgical laboratory, measurement of high temperatures and study of alloys (1); ore dressing.

Mineralogy.—Geometric crystallography (2); physical, chemical and descriptive mineralogy (3); determinative mineralogy with the aid of the blowpipe (1).

Drawing.—Freehand drawing (2); tracings and blue prints, flat tinting, working drawings (4).

Mechanical Engineering.—Strength of materials (4); constructive elements of machinery and of electrical apparatus; boilers (1); steam engine (3); measurement of power, indicator practice (1) and brake tests (1).

English.—Rhetoric (2); American literature (1); English literature (1); history of the English language; literary criticism; essays; oratory.

German or French.—Review of the grammar (3) and selections from the literature (2); technical readings (1).

Economics.—Elementary principles (1) and practical economic problems (1).

Religion.—Philosophy of the important religions of the world (1).

Thesis.—Work showing the student's ability to conduct a scientific investigation and report properly upon the same, the subject being in the field of electrochemistry.

COURSES BY YEARS.

Freshman Year.

First Semester.		*Second Semester.*	
Algebra and trigonometry	4	Elementary mechanics	5
Chemistry	2	Stoichiometry	2
Chemical laboratory	2	Qualitative analysis	3
German or French	3	Physics	2
Freehand drawing	2	Physical laboratory	1
Hygiene	1	German or French	3
English and essays	3	English and essays	2

SUMMER TERM (4 weeks).

Constructive Elements of Machinery and Electrical Apparatus.

SOPHOMORE YEAR.

First Semester.		*Second Semester.*	
Analytical geometry	5	Calculus	5
Physics	3	Physics	3
Physical laboratory	1	Physical laboratory	1
Drawing	3	Blowpipe analysis	1
Metallurgical constructions	1	Mineralogy	3
Crystallography	2	Drawing	1
English and essays	2	Metallurgical constructions	2
		English and essays	2

SUMMER TERM (4 weeks).

Mechanical Technology.

JUNIOR YEAR.

First Semester.		*Second Semester.*	
Chemical philosophy	3	Metallurgy	5
Quantitative analysis	3	Quantitative analysis	4
Advanced blowpiping	1	Steam engine	3
Electricity and magnetism	2	Electrical engineering	2
Dynamos and motors	2	Alternating currents	2
Electrical laboratory	1	Electrical laboratory	1
Strength of materials	4		
Boilers	1		

SENIOR YEAR.

First Semester.		*Second Semester.*	
Metallurgy	4	Metallurgical design	2
Quantitative analysis	3	Preparation of ores	3
Quantitative blowpipe analysis	1	Electrometallurgical processes	1
Electrometallurgical laboratory	1	Metallurgical laboratory	1
Measurement of power	1	Measurement of power	1
Dynamo laboratory	2	Dynamo laboratory	2
Electric stations	2	Electric transmission of power	2
Theory of electrolysis	1	Economics	1
Electrolytic laboratory	1	Philosophy of religion	1
Economics	1	Thesis	3

DISCUSSION.

THE CHAIRMAN: Gentlemen, we have listened to Professor Richards' paper with interest. It is now open for discussion.

We have with us a number of representatives of the higher educational institutions, and I hope the discussion will be quite an interesting one.

Dr. W. D. Bancroft: Mr. Chairman, we do not have, at Cornell, distinct four-year courses in chemistry and in electrochemistry; but we have been working along lines very similar to those outlined by Professor Richards. For students going into industrial chemistry, we outline a four-year course in which the studies of the senior year are optional. We throw geometry and trigonometry back into the preparatory schools and take up analytical geometry and the calculus in the freshman year. The rest of the freshman year is devoted to introductory chemistry, qualitative analysis, physics, and German or French. In the second year the students have quantitative analysis, organic chemistry, assaying, gas analysis, spectroscopic analysis, and mineralogy. In the third year they have introductory physical chemistry, electrochemistry, mechanics of engineering, mechanical drawing, physics, and advanced quantitative analysis.

Those students who wish to specialize in electrochemistry would take a laboratory course in this subject during their senior year.

This course covers very much the same ground as that in the paper just read. I am not certain that we have quite as much machine design and I think that there is less metallurgy; but the general principle is the same.

Prof. Albert W. Smith: Mr. Chairman, from experiments made at Case School in Cleveland, we have there adopted a course very similar to that which Professor Bancroft described as in use at Cornell. We have not a special course in electrochemistry, but this work has been connected with the course in metallurgy and chemistry, and it departs and is different from what Professor Richards has outlined in offering more advanced chemistry, with perhaps a little more attention to steam engine work. With those exceptions, the work at Cleveland is the same as that outlined by Professor Richards, and it has been in practice now for two years.

Dr. H. S. Carhart: Mr. Chairman, we have no course distinctly electrochemical at the University of Michigan, but we have a course in chemical engineering and a very well developed course in physical chemistry. I think it is quite likely that out of these will grow, in the near future, a course in electrochemistry somewhat as outlined by Professor Richards. I have only one or two remarks to make upon his paper. The course appears to me to be a very good one; perhaps a little overcrowded on the chemical

side. It makes room for certain studies which, it seems to me, have no relation to electrochemistry, though they are all very good in themselves; such as rhetoric and English literature and the philosophy of religion. They might perhaps be left out in order to make room for other studies, which have a definite relation to electrochemistry.

Trigonometry, I believe, is quite generally required for admission to engineering schools; but certainly I am in accord with the ideas presented in the paper, that elementary physics should be required as a preparation for entering this course; unless I am mistaken, physics for admission is not required at all at Cornell.

Dr. Bancroft: It is required.

Dr. Carhart: It is not, in general.

Dr. Bancroft: Not in general. The general opinion among chemists is that the teaching of physics in schools is rather better than the teaching of chemistry. Of course you, as a Professor of Physics, might hold the opposite.

Dr. Carhart: No; I think that is quite correct. But that appears to be, in part, the objection. But I think we ought not to crowd too much in the high schools, and perhaps the mathematical work will be done better in the colleges than in the high schools, with the exception of trigonometry.

Prof. C. F. Burgess: At the University of Wisconsin our experience has been somewhat different from that just expressed. Our course in electrochemistry has been an outgrowth of the electrical engineering department. For the past seven or eight years we have been giving instruction in applied electrochemistry and have gradually added certain elective studies such as analytical chemistry, physical chemistry, etc., for those desiring to specialize in this line. A year ago we instituted a four years' course in applied electrochemistry on the same basis that four years' courses in other engineering lines are given; and the course we have now is very similar to that which Professor Richards has outlined. We, however, do not devote as much time to metallurgy.

The principal difficulty in designing a course for electrochemical engineers, and one which seems to me is not overcome in the outline given in the paper just read, is getting all the essential studies in the four years and treating them as thoroughly as they should

be treated. A great deal of the work, in fact, the majority of the work, has necessarily to be done in the laboratory, and with even fewer studies than indicated, the time of the student is thoroughly taken up.

There have been differences of opinion expressed in technical periodicals, and some difference of opinion expressed here to-day, as to the amount of pure chemistry and physical chemistry which should be given with such a course. It seems to me that in talking on this question we must first decide whether the product is to be an electrochemical engineer, or an electrochemist. The same distinction must be drawn here as is drawn in the training of the chemist and chemical engineer. An electrochemical engineer must be, primarily, an engineer, and it seems to me his training should be acquired by taking an engineering course. That is the object we have had in view—to make the student primarily an engineer with a training in such lines of chemistry and electrochemistry as will enable him to use the combined knowledge to the best advantage.

Dr. Bancroft: Mr. Chairman, the last distinction made by Professor Burgess is a perfectly sound one, and we are having that made, to a certain extent, at Cornell. I did not refer to that a moment ago because I was speaking more especially of the people who are primarily chemists. But the course for engineers in Sibley College is the same for all during the first three years, and in the senior year they decide whether they are going to specialize in electrical engineering or mechanical engineering. We are now trying to get a certain number of those to take as much electrochemistry as we can give them, the idea being they are primarily engineers and that they should learn enough about the chemical side of electrochemistry so that they shall be able to work more or less intelligently, but always primarily as engineers. The other course I outlined was more especially for men who intended to be, primarily, chemists, and was intended to apply more especially to the chemical side of electrochemical processes. Of course, as they differentiate the chemical side of a process from the engineering side, they must know a certain amount of engineering. But you have those two sides: one is a man who is primarily an engineer and knows enough of chemistry, especially electrochemistry, so that he can work intelligently. The other man is

primarily a chemist and he knows enough of engineering so that the dynamo and machinery are not a sealed book to him. These two will always be more or less separate, although the difference will vary very much in individual cases. But I am quite in sympathy with the idea that there are two distinct professions, one of the engineer and the other of the chemist.

Dr. C. A. Doremus: If I may add a word or two from the Chair, I would say I fully concur with what Professor Richards said in regard to the study of higher mathematics. The question has been raised as to the number of studies that could be introduced in a course. The curriculum of the College of the City of New York had for many years the integral and differential calculus in the sophomore year. Every student of the college was obliged to study the higher mathematics. Experience has shown that it is wise to postpone the study to the junior year, and that the study should be given only to those who are to receive a more scientific training. The age still remains about seventeen or eighteen.

In regard to the electrochemical part, I feel, personally, that too much stress in Professor Richards' course has been laid upon the metallurgy and too little upon the organic chemistry. My own personal experience in the last few years has shown me that there is no sharp line of division between inorganic and organic chemistry. The student or engineer to be proficient in his work in the course ought assuredly to include the broader outlines of organic chemistry. The possibilities of experimentation should be shown the student. When we consider that the investigation of the carbides has done much to elucidate the petroleums, that the manufacture of calcium carbide and of acetylene is going to be an introduction perhaps to that of a great many compounds, it is not necessary to go further. I think that the topic of the influence of the electric discharge at high potential has also been omitted. This is a field which I am sure in the very near future is going to be very much developed and will be of the very greatest importance.

President Richards: I would say, in answer to Professor Bancroft, that the course is made of four years to correspond with other courses of four years, in civil engineering, mechanical engineering, chemistry and metallurgy, and that it is designed to take its place as an undergraduate course with the same entrance re-

quirements as the other technical courses; and therefore it is not possible to put the mathematics back into the high schools even if that were desirable. For myself, I think it is a dangerous precedent to try to get too much mathematics from the lower schools, as the teachers there do not teach it in the thorough way that it is taught from the university standpoint, and by making the entrance too high we get out of touch with the preparatory schools.

Profesor Bancroft also remarks as to the electrochemical engineer. I agree with him as far as concerns the electrochemical engineer. My paper was primarily upon the course of electrochemistry, and I would lay down as a thesis there that the electrochemist should be primarily a chemist and should not be left to pick up the elements of any chemical steps in his junior or senior year, but he should get them as early in his course as we can give them to him.

Professor Smith has spoken of the increased amount of theoretical chemistry and steam engine which is given in their course—both of which are very desirable additions—but I felt that I put as much into the course in both of those lines as could possibly be compressed into it.

In regard to Professor Carhart's remarks: a university course, I think, is always overloaded. It is a continuous struggle between the different professors in different departments to get as much time as they can for their specialties, and it is the greatest burden or difficulty in outlining a course, to compress it within reasonable limits. The amount of work I have assigned here amounts to seventeen or eighteen hours a week, an hour being an hour's lecture or two hours' work in drawing or blowpipe laboratory, or three hours' work in the physical laboratory or chemical laboratory, and in that respect it is not overloaded in comparison with the other courses in metallurgical, civil, mining and mechanical engineering.

The introduction of rhetoric and literature and the philosophy of religion in all our courses is to give a man a little breadth and to keep him from getting to be a narrow specialist, and I am in sympathy with the idea of putting some of these broad culture studies into our courses in the university, even at the expense of cutting down some of our distinctly technical subjects in so doing.

Professor Burgess has remarked about the course in metallurgy.

I think we are perhaps forgetting that the rise of electrochemistry as an industrial art has been practically from the metallurgical side. I do not agree with Professor Burgess that there is too much metallurgy given in this course. It is the same as is given to our chemical students and the metallurgists, and in the course in mining engineering.

In regard to Professor Doremus' remarks: the calculus has been put in at the close of the sophomore year, and with our students this has been found quite practicable, as they average eighteen and a half years on entering and twenty-two and a half years on leaving, and we find our students at the end of their sophomore year, being then twenty years old, easily able to take the subject of calculus.

The criticism in regard to the omission of organic chemistry I admit is a proper one and is one I would like to remedy. I would like to put in the broad outlines of organic chemistry, if it could be done without leaving out some other things which I think should more reasonably be included. I think that organic chemistry can easily be approached, however, by a man who is in training in inorganic chemistry and analysis and chemistry in general; and that has been left out of our course as it stands here,—although in a perfectly balanced electrochemical course, I agree that it ought to be included.

A paper read at the Inaugural Meeting of the American Electrochemical Society, Philadelphia, April 4, 1902, President Richards in the Chair.

GRAPHITE ELECTRODES IN ELECTROMETALLURGICAL PROCESSES.

By Clarence L. Collins, 2nd., E. E.

The fundamental principle underlying most electrometallurgical processes is the reduction by carbon at high temperatures of the oxide of the material under treatment. The presence of some form of carbon and its consumption are therefore essential; but that carbon should also be chosen as electrode material is more from the necessity of the conditions to be met with than from choice. Although a good conductor and infusible at the high temperatures attained, it is by no means the ideal material, and its rapid consumption when exposed to oxidizing action is in many instances a serious difficulty with no obvious remedy.

Although necessary both for reduction purposes and for use as electrode material, it does not follow that the carbon essential for the reduction of the oxide should be supplied by the consumption of the electrode, for in practically all processes the consumption of the electrode, its burning away or oxidation, can be reduced to a minimum by a proper treatment of the conditions of the process and the materials in question.

All forms of carbon oxidize, but the temperature of oxidation of the various forms ranges between widely different limits. Thus amorphous carbon is consumed when heated in oxygen at from 370° to 385° C., whereas artificial graphite manufactured in the electric furnace burns at about 660° C.[1] The choice, therefore, of two forms of carbon having totally different temperatures of oxidation can easily be accomplished, and it is the practical application of this fact which has a very important bearing on the subject in question. In fact the various forms of carbon furnish almost as much possibility for what might be termed "selective" oxidation, as elements of totally different character.

For example, upon heating a mixture of an oxide and some

[1] "Recherches sur les Différentes Variétés de Carbone," *Le Four Electrique*, H. Moissan.

form of amorphous carbon, both being in the granular or powdered condition, at a certain definite temperature reduction occurs and the carbon is consumed. In a mixture of the same oxide and graphite, under otherwise similar conditions, the same action takes place but at a higher temperature, and the rate of consumption of the graphite at this higher temperature is practically the same as that of the amorphous carbon above. If both are present in the mixture, however, and in equal quantities, thoroughly mixed, a new relation is established. The oxygen in the presence of two forms of carbon naturally shows a decided preference for the amorphous carbon as against the less oxidizable graphite. Even at a much higher temperature than that necessary for the reduction of an oxide in the presence of graphite alone, the preference is still evident in the higher rate of consumption of the amorphous carbon.

This same reasoning may be extended to the conditions to which electrodes are subjected in actual electrometallurgical work. In fact, in the case of the mixture mentioned above where two forms of carbon were present, we may consider the electrode as one form, the other being that added to the oxide in the granular or powdered form for reduction purposes. This is actually the case at the surface of the electrode where it is in contact with the oxide or mixture, and as this is where the whole electrode consumption takes place, it affords a proper comparison. The oxygen here set free has the choice of either the carbon of the electrode or that of the mixture. If both are equally resistant to oxidation, both are equally consumed, but if one is more incombustible than the other, a preference is at once shown and there is a saving of the one at the expense of the other. The electrode is the form of carbon in which it is most desirable to have the smaller consumption, not only on account of its greater first cost over that of some cheap granular or powdered carbon, but also on account of the loss in efficiency always incurred in interrupting the furnace operation, the cost and labor of renewals, and the waste of the electrode ends. It is, therefore, evident that, in order to obtain the minimum electrode consumption, some form of carbon must be chosen as electrode material highly resistant to oxidation—such as graphite—and the use in the mixture for reduction purposes proper of some easily consumed carbon—such as charcoal or coke. Where no other carbon is pres-

ent, the substitution of a graphite electrode for one of amorphous carbon evidently offers no material advantage except in the lower rate of oxidation where exposed red hot to the air above the surface of the materials treated. It is by the proper utilization of two forms of carbon with widely different properties that the greatest economy can be shown.

If it were possible to obtain an absolutely uniform temperature throughout a mixture of an oxide and amorphous carbon, using graphite electrodes, the temperature could be regulated to that necessary to cause the reduction of the oxide by the amorphous carbon alone, and at that temperature there would be no consumption whatsoever of the electrodes. But in actual practice, although selective oxidation may be approached and very much increased efficiencies attained, it is absolutely impossible to obtain a uniform temperature throughout a mass of material due to unequal conditions of radiation and conduction, and the higher temperatures of points of contact of the individual particles. If the material is thoroughly mixed and in a fine state of subdivision, this condition can be approached, but in some cases there are other practical considerations which prevent even this recourse.

The high electrical conductivity of graphite electrodes furnishes an additional and very important factor of economy. On account of this property electrodes of from one-third to one-fourth the cross section of those necessary with amorphous carbon articles may be used, not only reducing the weight per unit of length and decreasing the surfaces exposed to any oxidizing action, but also causing less loss due to heat conducted from the center of the furnace through the electrodes themselves. This property alone—that of greater conductivity—is enough in itself to cause a saving in the use of graphite electrodes, even were the temperature of oxidation no higher than that of the amorphous carbon articles.

Another characteristic of graphite, and one which introduces still other important factors into the practical use of such electrodes, not applicable to amorphous carbon articles, is ease of cutting, or machining. Machine work can be done upon graphite electrodes, manufactured by the Acheson process, even more readily than upon the softest iron, and with as great a nicety and finish. This fact affords many suggestions in regard to the assembling of two or more pieces, which has proved of practical

utility and economy in many lines of both electrolytic and electrometallurgical work.

This assembling is seen in its simplest form in the joining of two round electrodes by a threaded joint, as represented in partial cross-section in Fig. 1. Actual test has shown that the two ends, if faced off, can be drawn up tight, the whole forming practically one solid electrode with very little, if any, increased resistance where joined. Such a joint has many applications. In

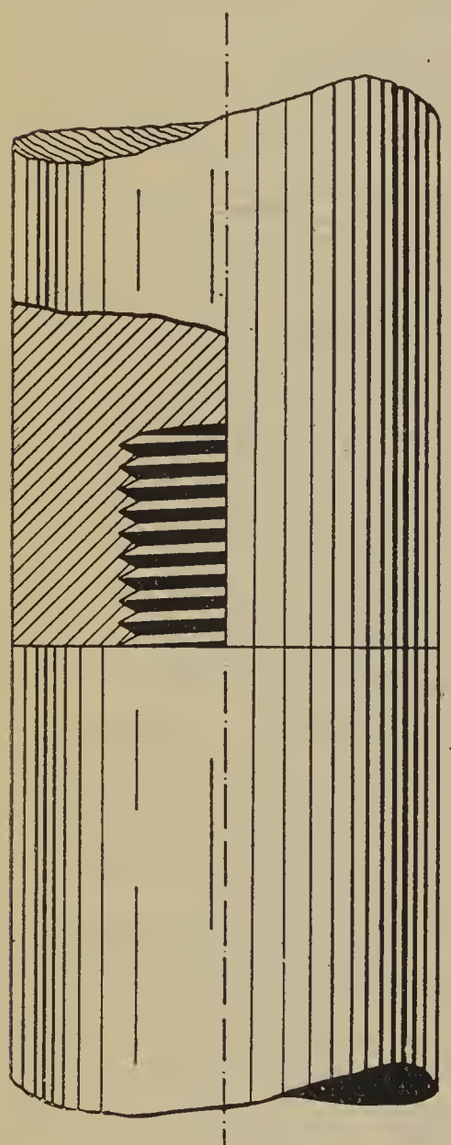


FIG. 1.

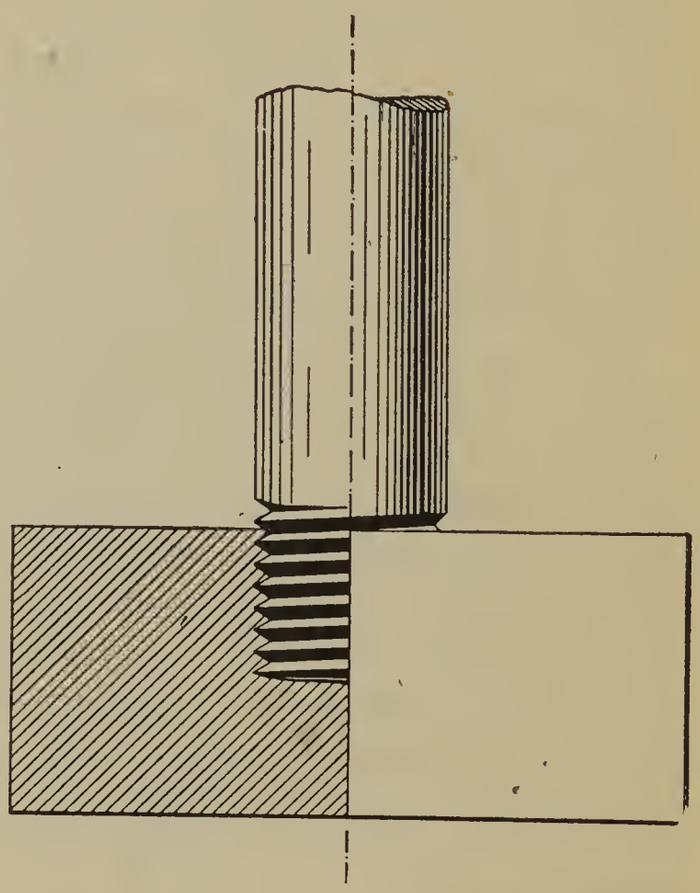


FIG. 2.

some processes a furnace has to be shut down to renew electrodes. If the joint shown in Fig. 1 is used, and some form of clamp or collar contact with the metal conductors applied, a new electrode can be joined to the end of the one in use, and these fed into the furnace one after another as necessary. There are then no electrode "butts," or ends, to be thrown away or to be ground up for use in place of a much cheaper granular carbon.

If such a method of feeding in electrodes is not applicable to the process in question, a jointed electrode can be used, one part of which is *permanent* (that fastened to the metal conductors), the other being the *working* electrode. The latter may be renewed as it becomes necessary, and can be consumed practically up to the joint itself. In this case, also, there are no butts or ends. Furthermore, the permanent part can be as long as desired, removing the metal conductors far from the hot parts in the furnace and entirely doing away with the necessity of the many complicated forms of water-cooled contacts which have been devised. In Figure 2 a similar joint is shown between a rod and a slab or block. This is used to obtain large areas of maximum heating with a minimum of electrode weight and consumption.

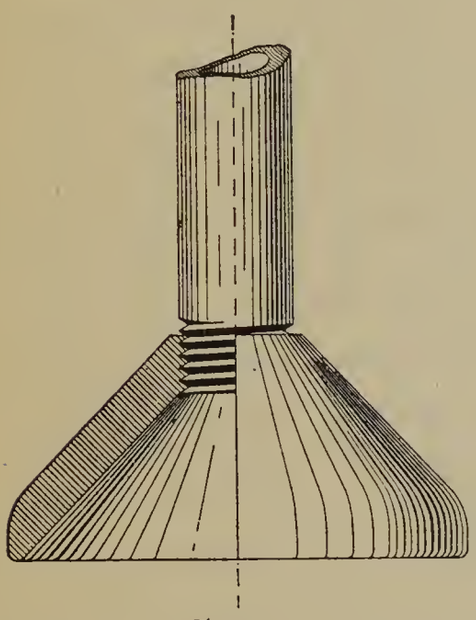


FIG. 3.

FIG. 4.

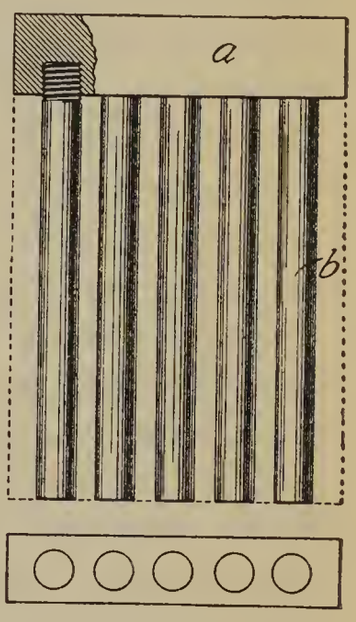


FIG. 5.

Fig. 3 shows an electrode in the form of a hollow tube threaded into a hood. Although this form is serviceable principally in electrolytic work as either anode or cathode for the collection of gases, it may also be used in electric furnace operations where it is desired to conduct some inert gas into the center of the furnace, or where some vaporized product is to be carried over into a condensing chamber.

In Fig. 4 an end view is shown of two slabs which have been dovetailed together along their long, narrow edges. Such a method of assembling can be used in forming partitions, walls, or linings to furnaces, or in the assembling of slabs into box forms for the collection of molten metals or fused salts, the box

if desired acting as one of the electrodes in the process in question.

On account of the tendency to develop electric furnaces of very large capacity, utilizing very powerful currents and having large areas of maximum heating, it is necessary to devise some form of electrode of large size, an electrode which will have ample carrying capacity and be a solid, compact mass, capable of resisting oxidizing action to a high degree. In some cases this is done by using a number of electrodes of smaller cross-section, clamped or fitted to one common terminal. One objection to this is the breakage in the furnace of one or more of these single electrodes, especially when used in long lengths. In Fig. 5 a form is suggested which it is thought would have practically the carrying capacity and resistance to oxidation of a graphite electrode, but would be less expensive than if the same section were made up entirely of smaller electrodes. In this figure *a* represents the end of the electrode to which the conductors are to be attached. It consists of a solid graphite slab of any desired size running across that end of the electrode and affording a firm, solid contact or means of support. Into the under side of *a* are threaded a number of rods *b*. These give the desired length to the electrode. Within the space indicated by dotted lines and around the rods a mixture of fine granular graphite and pitch is then tamped or molded under pressure, giving a solid rectangular form to the assembled mass. The whole is then placed in some form of furnace and the pitch bond carbonized. The resulting electrode possesses high electrical conductivity along its length, has ample strength, and should resist oxidizing action to a high degree.

In Table I, the results are given of some experiments with amorphous carbon and graphite electrodes in actual electro-metallurgical work. The amorphous carbon electrodes were of the best American manufacture, made in the usual manner of finely ground petroleum coke with a pitch bond. The graphite electrodes were furnished by the International Acheson Graphite Company of Niagara Falls, N. Y., and were of great purity and high electrical conductivity. The specific resistance was only 0.00032 ohm per cubic inch, or about one-fourth that of the amorphous carbon articles.

TABLE I.

Series.	Number, size and kind of electrodes used in each terminal.	Total current in amperes.	Current density amperes per square inch.	Average hours run.	Average length consumed.	Number of runs.	Relative weight consumed per hour.
A	Four-4″ × 4″ × 24″ Amorphous carbons.	4000	62.5	8	12″–14″	4	1.000
B	Four-4″ × 4″ × 24″ Acheson graphite.	4000	62.5	32	12″–14″	4	0.250
C	Four-2″ × 4″ × 24″ Acheson graphite.	4000	125.0	32	12″–14″	15	0.125
D	Four-2″ × 4″ × 30″ Acheson graphite.	4000	125.0	95	22″–24″	15	0.074

In all the experiments the electrodes projected into the mixture under treatment, and were not only exposed to its oxidizing action, but were also exposed to some oxidation from the oxygen of the air above the surface of the mixture. All the runs were under as nearly as possible identical conditions.

The two series A and B give the comparative results obtained using electrodes of the same cross-section in both cases. In the latter instance the graphite electrodes show an efficiency four times as great as that developed by the amorphous carbons. Comparing B and C in which the cross-section of the graphite electrodes has been halved, little increase in length of life is shown, which may be explained by the fact that as the electrodes in all cases were ranged side by side touching each other, in the latter instance touching along their two-inch faces, the total surface exposed in both cases was approximately the same. In C, however, the weight consumed per unit of length has been halved with a corresponding further increase in economy.

In A the amorphous carbons were slightly heated by the current density used, whereas in C with twice the current density the graphite electrodes showed no sign of heating whatsoever. Comparing A and C it is seen that in the process in question the graphite electrodes developed an efficiency eight times as great as

that shown by the amorphous carbon articles. As the cost is only about three times as great the economy of the former is very evident.

In the series D the graphite electrodes were partially protected by a casing from the oxidizing action of the air above the surface of the mixture and a still further increase in efficiency was obtained. This means of protection, however, was not possible with the amorphous carbons on account of the heating developed in the carbons themselves. To utilize such a protection it would have been necessary either to increase the number of the electrodes, or to cut down the current density in the amorphous carbons with a corresponding loss in the capacity of the furnace. With the current density one-half that given in A, the length of life of the amorphous carbon electrodes begins to approach that shown in D. But with such a decrease in the capacity of the furnace, other costs are increased per unit of output, and this more than offsets any gain in electrode consumption.

In making a test between amorphous carbons and graphite electrodes, a fair comparison can be obtained only by the utilization of the full carrying capacity of each with equal electrical losses in the electrodes themselves. The difference in the temperatures of oxidation of the two, although marked, is in some cases not in itself sufficient to cause a great difference in their action. The problem is not one of mere substitution of graphite for amorphous carbon with a resultant economy. The greater heat and electrical conductivity of the graphite electrodes must both be taken into consideration. Although there is probably no electrometallurgical work where a saving cannot be effected in the use of graphite electrodes, this saving can only be obtained by a proper treatment and a full realization of *all* the properties of the two materials in question.

DISCUSSION.

Mr. Henry Howard: Mr. Chairman, I would like to ask Mr. Collins how graphite compares with amorphous carbon in length of life in chlorine work.

Mr. C. L. Collins: In the electrolysis of chloride solutions the life of the graphite electrode is over twelve months, whereas amor-

phous carbon lasts from thirty to ninety days, depending a great deal upon the surface current density used and the conditions of the process in question.[1]

Mr. N. M. Hopkins: Mr. Chairman, I would like to ask Mr. Collins how the carbons are protected from oxidation outside of the furnace.

Mr. Collins: Above the surface of the materials treated, a sheet iron casing surrounded the electrodes. A mixture of ground coke and pitch was tamped in between the casing and carbons. This mixture carbonized, upon heating, and protected the carbons to a large extent from oxidizing action. The sheet metal burned away as the electrode itself was consumed.

Dr. N. S. Keith: Perhaps it is not pertinent to the subject under discussion, but I am very desirous of obtaining some knowledge as to the use of these graphite electrodes in electrolyzing solutions. I have been very desirous of obtaining an anode that will be practical and cheap. The one difficulty I have found in the use of amorphous carbon anodes is first, their very rapid destruction, and second, the impurifying of the solution by the introduction of floating carbon, or, perhaps, some dissolved carbon. I have not determined whether there is any such thing as dissolved carbon in electrolytic solutions, but I have found in such solutions, when using graphitic anodes, more or less floating carbon; the solution became darkened very much, and there was a deposition, not simply of falling or adhering carbon, but a deposition of carbon covering the copper surface of the cathode and, finally, enclosure of the carbon in the copper. It is a difficulty which we overcame simply by the use of lead anodes in sulphate solutions. But lead anodes as insoluble or permanent ones in chloride solutions do not seem possible.

Mr. D. H. Browne: Mr. Chairman, I think I can answer Dr. Keith's question in a very satisfactory way. At The Canadian Copper Company's works at Brooklyn we are using anodes made by the Acheson process. These anodes are 26 inches in length, and in cross section one by four inches. We have been using these in electrolyzing nickel chloride, and we have also tried them in the electrolysis of common salt, and also incidentally in sulphates.

[1] For further particulars I would refer to the Zeitschrift für Elektrochemie, VIII, No. 10, pp. 143–147, 1902. Also same, VII, pp. 971, 987, 1012, 1027, 1071, 1083.

I wish to say that in sulphate solutions we have never had any satisfactory life of a carbon anode, but in the chloride solutions I have been using this Acheson graphite for over three years, and I can show you carbons which have been used for three years under a current density of from 50 to 250 amperes per square meter, and the edges are just as sharp as the samples which you see on the desk. We have found them absolutely intact after three years' service. The only fault I have to find is that some made by the National Carbon Company were somewhat porous, and these pores remain after the carbon has been converted into Acheson graphite. In order to stop these pores we immerse the carbon in boiling paraffine, after which treatment the pores give no trouble. In my opinion, for working in chloride solutions no carbon anode can equal the Acheson graphite.

Dr. Keith: That is correct so far as a chloride solution is concerned, but in electrolysis it is very desirable that we may obtain an enduring anode by means of which we can electrolyze sulphate solutions. I quite agree as to the endurance of the anodes in chloride solutions.

Mr. Hering: I tried both graphite and the plain carbon as anodes in the oxidation of chromic acid solutions and found that neither of them would stand at all.

Mr. Collins: In reference to the use of graphite electrodes in sulphate solutions, they are not recommended for such work, as the disintegration is very rapid. Although the graphite electrodes still show up better than the amorphous carbons, the difference between the two is not as marked as in other lines of work. The oxidizing action, which causes most of the disintegration of the electrode, is much more severe.

The use of paraffine to overcome difficulties due to the porosity of the electrodes has been mentioned. It is impossible to manufacture an electrode without some slight internal checks, and on account of these checks and its porosity, there is a creeping of the solution up through the electrode which, together with the gases generated, in some cases causes corrosion of the metal conductors where contact is made. This difficulty can be overcome by impregnating the electrode with paraffine. The electrode is stood up on end in a dish of melted paraffine, and the paraffine allowed to

soak up to any desired distance. The surfaces of contact are afterwards scraped to remove the paraffine on the outside.

I am sorry that I am not at liberty to give the nature of the mixture in which the comparative tests shown in Table I were made. The results were obtained in actual electrometallurgical practice upon a large scale, but the company making them desired its name withheld. As far as the principles of the tests given are concerned, however, it might be any form of mixture in which reduction of an oxide takes place, such as mixtures of carbon and silica, carbon and lime, carbon and alumina, etc., with any necessary fluxes.

A paper read at the Inaugural Meeting of the American Electrochemical Society, Philadelphia, April 4, 1902, President Richards in the Chair.

NOTE ON THE GLADSTONE-TRIBE COUPLE.

By Wilder D. Bancroft.

In 1872 Gladstone and Tribe invented the zinc-copper couple, which is usually called by their name. In its most effective form it is prepared by dipping zinc foil into a copper sulphate solution, rinsing, drying, and heating the mixed zinc and copper to a temperature just below that at which brass would be formed. With this couple one can do a number of interesting things. It will reduce chlorates completely to chlorides and nitrates to ammonia. With ethyl iodide, one gets 95 per cent. of zinc ethyl. Chloroform can be changed to acetylene, and benzyl bromide to dibenzyl, to mention merely a few of the organic compounds which can be prepared by means of it.

While the action of the couple is clearly electrolytic, as is shown by the varying intensities of couples made of other pairs of metals, no one has ever reproduced the phenomena when using a voltaic cell. This is the more unfortunate since the couple in its usual form is not adapted to efficiency measurements, and since one cannot study the effect of varying current density, for instance.

We have recently succeeded in duplicating some of the results of Gladstone and Tribe electrolytically, using a pair of zinc plates or a pair of copper plates and an external source of current. We have had no difficulty in decomposing chloroform between zinc plates in an alcoholic solution at a temperature of about 60° C. At first, the resistance is very large and only a few milliamperes pass even when the plates are close together and there is a potential difference of 100 volts. With increasing formation of zinc chloride, soluble in alcohol, the current increases very rapidly. So far we have only made qualitative experiments on this reaction, but it will be studied in detail before long.

Working at about 93° with copper electrodes, we find that potassium chlorate can be reduced readily to chloride. We are

now studying this reaction quantitatively to determine the effect of concentration, current density at the two electrodes, temperature, and alkalinity. We use a revolving anode to keep the solution stirred, and finely divided copper oxide is formed, most of which separates from the electrode. We have taken a five per cent. solution as the normal one, that being practically saturated at ordinary temperature. As a rule, we have run four amperes for two hours, though changes have been made in the amount of current and the time.

The current yield increases with the current density at the anode, and is practically independent of the current density at the cathode. Addition of caustic potash decreases the efficiency. The reduction decreases with falling temperature, and also with decreasing concentration after one gets below a certain limit. The efficiency is much less with a 1 per cent. solution than with a 5 per cent. solution; but there seems to be no difference between a 5 and a 40 per cent. solution. Special experiments have shown that there is no appreciable reduction when the potassium chlorate solution is heated with copper and copper oxide without the passage of a current. There is also no reduction when potassium chlorate and copper sulphate are heated together, so that a possible instability of copper chlorate is not to be feared.

In calculating our percentage yields, we started with the hypothesis, that to remove three atoms of oxygen from one molecule of potassium chlorate required the supply of six atoms of hydrogen or their equivalent. In other words, that we should have 100 per cent. efficiency if we obtained one molecular weight of potassium chloride for every 6×96540 coulombs supplied. This is the proper basis of calculation in the case of the electrolytic oxidation of potassium chloride to chlorate. Calculating on this basis, however, we get efficiencies of 180 per cent. Our experiments are still too incomplete to enable me to tell what reaction actually takes place; but I can call your attention to one or two possible explanations. The amount of copper oxide corresponds very closely to the quantity of electricity, so that there is no possibility of copper dissolving as cuprous salt. When the reaction first starts, there is evolution of hydrogen at the cathode, but this practically ceases as soon as there is copper oxide diffused through the solution.

There is no doubt in my mind but that the oxygen for the

copper oxide comes from the potassium chlorate. For every two equivalents of copper going into solution, we should have two of hydrogen set free, which might also reduce. This could be written

$$3Cu + 2KClO_3 + 3H_2 = 3CuO + 3H_2O + 2KCl.$$

This would mean a possible efficiency of 200 per cent. If we assume that KClO decomposes spontaneously into KCl and O in presence of copper oxide, we should have a possible efficiency of 300 per cent. If one assumes spontaneous decomposition of the chlorite $KClO_2$, a still higher apparent efficiency is possible. I hope, before long, to be able to decide definitely between these hypotheses. To-day, I wish only to call your attention to the fact that we have taken the first step towards replacing the Gladstone and Tribe couple by an electrolytic process, and that it seems possible that we can do electrolytic reductions in organic and inorganic chemistry with a much higher efficiency than has usually been obtained by purely chemical action.

DISCUSSION.

Mr. C. P. Townsend: Dr. Carl Luckow, of Cologne, has proposed a method similar to this for the commercial production of copper oxide. Copper electrodes are suspended in a chlorate solution, into which air is injected. Under these conditions, and probably owing to the injection of air, no reduction of the chlorate occurs; on the contrary it is said that the yield of copper oxide is quantitative, and that no reduction products are formed.

Mr. W. McA. Johnson: The chlorate temperature is given, is it not, as 90? I think it would break up into chlorine and chloride.

Mr. A. T. Weightman: Is it due to a catalytic action of the oxide on the chlorate? Various metallic oxides are known to have the property of decomposing chlorates without undergoing any change in themselves, due presumably to a catalytic effect.

Mr. H. H. Dow: Professor Loomis refers to that reaction and speaks of the change at high temperature, into chlorate. There is a loss of something like one-third, as I remember it. So that would account for the large yield. That is, this would be a loss of about one-third of the oxidizing quality.

Dr. W. D. Bancroft: I was not aware of the formation of copper oxide in that way, but we do get a quantitative yield here. I am inclined to think, myself, that with the blowing in of air at ordinary temperatures there would be practically no reduction, and it would be found perfectly satisfactory for copper oxide.

As regards the catalytic action, it has already been shown that copper oxide and cobalt oxide do decompose hypochlorite. The temperature is not the essential factor, because if we substitute platinum electrodes for copper electrodes there is very little reduction. One of the essential features is the use of the copper anode as against the platinum anode. We have made one preliminary experiment with zinc electrodes instead of copper electrodes, and while there is a very marked reduction, it seems probable that the reduction is much less with zinc electrodes, than with copper electrodes. Whether that is due to the superior catalytic action of copper oxide as against zinc oxide, or whether to the fact that zinc oxide is somewhat more soluble, I do not know. Our experiments show that there is a deoxidation at the anode; that is, that the reduction is not entirely at the cathode. At first, before there is any copper oxide present, hydrogen is given off at the cathode; but after that practically no hydrogen is set free.

Whether it is to be considered as used up electrolytically or by combining with spontaneously decomposing chlorite or hypochlorite is a question which will have to be settled by experiments.

Mr. Weightman: Have you examined, chemically, the gases evolved at the anode and cathode. An excess of oxygen beyond that which would be liberated by the current would indicate that a decomposition of the chlorate was taking place and not a true reduction.

Prof. Bancroft: The cell has been kept in a water-bath at approximately 90°-93°. With a current of not over 4 amperes, I doubt whether the temperature of the electode is very much above the temperature of the electrolyte. Of course it might be two or three degrees, but it can be hardly more than that.

A paper read at the Inaugural Meeting of the American Electrochemical Society, Philadelphia, April 4, 1902, President Richards in the Chair.

THE NASCENT STATE.

By C. J. Reed.

The "Nascent State" is defined as the condition of a substance immediately after its component atoms have been set free from one combination and before they have entered into a subsequent combination either with themselves or with the atoms of another substance. The existence of matter in such a state, and the existence of peculiar properties appertaining thereto, has been a popular and convenient assumption for about a century past. This assumption has served certain purposes long and well, and is entitled to all the reverence that comes with age and usefulness. But, as with other superannuated beings, when it has outlived its usefulness, it should be quietly deposited where it will slumber inoccuously.

This venerable assumption has at divers times served as a convenient hiding place, behind which philosophers have been able to conceal the ignorance that always precedes experiment and investigation.

Whenever a phenomenon is encountered in chemical or electrochemical reactions, that cannot be readily accounted for by the existing theories, it is much more satisfactory and convenient to use such an expression as *status nascendi* than the term *ignorance.*

This assumption of a nascent state has also served admirably as a sort of elastic plug for filling up holes in certain theories, which are otherwise inconveniently translucent.

While this assumption of peculiar powers and properties appertaining to the nascent state has been very useful for the purposes named above, it does not appear in any of the records of a century of experimental progress that such an assumption is either required by, or of assistance in explaining, experimental facts. No substance in the so-called nascent state has been shown to possess powers or properties different from the powers it possesses in the most ordinary state. The supposed difference between the nascent state and the ordinary state appears to be founded in all

cases entirely upon coincidences, which have been mistaken for causes.

In the time allotted to me it would not be possible to consider the experimental evidence covering all cases of alleged nascent activity. The substance of most general interest in this connection is the so-called nascent hydrogen, that being the substance most frequently called upon for the peculiar duties of a nascent substance.

The supposed function of nascent hydrogen has always been that of reduction of some other substance, in contact with which the hydrogen is generated; while the supposed function of nascent oxygen has always been that of oxidation of some substance, in contact with which the nascent oxygen is generated.

It is in electrochemical reactions that hydrogen and other *nascent* bodies are most frequently generated in contact with other reducible or other oxidizable substances. It will probably be admitted, however, that whether the nascent hydrogen be generated electrochemically or otherwise, it is itself always generated by the process of reduction and by a reducing agent acting at the same point where the nascent hydrogen is supposed to exert its peculiar nascent power. That is to say, the nascent hydrogen is always born of a reducing power, and the nascent child, in turn, at the very instant of its birth and by reason of its nascent condition, becomes itself a reducing power; and in acting as a reducer it simultaneously ceases to be nascent hydrogen by becoming oxidized.

It will be admitted that no hydrogen can act as a reducing agent and also appear either as free or as nascent hydrogen. Hydrogen, whether nascent or ordinary, can act as a reducing agent only by ceasing to be free hydrogen, that is, by undergoing chemical combination. Any hydrogen that succeeds in escaping from a chemical reaction in the free state could have had no more reducing power than hydrogen not present. There is probably no one in this audience, who will contend that any chemical reducing agent can exercise a reducing action without itself undergoing chemical change, and if the reducing agent is a free element, it must undergo combination, the only reaction of which it is capable.

If, therefore, hydrogen under any circumstances exercises a reducing action in its nascent state, it is not possible for us to ob-

tain any direct ocular or experimental evidence of that fact; since any hydrogen which acts in such a manner could not possibly appear in the free state, could not become visible, or give any evidence that it takes part in the reaction. What we do have experimental evidence of is, that certain chemical reductions do take place simultaneously with and in contact with the reduction of hydrogen to the free state. But are we justified in saying, simply because two bodies in juxtaposition undergo simultaneous reduction under the influence of the same reducing agent, that one of these bodies reduces the other? If so, how are we to determine which of the two reduced bodies has reduced the other, or why they were not both simultaneously reduced by the original reducing agent?

If a certain reducing agent, *A*, when added to a chemical system, results in the simultaneous reduction of both *B* and *C*, we know therefrom that the chemical energy of *A* is greater than that of either *B* or *C*; but there is no evidence in this result as to the relative energy or reducing power of *B* and *C*. For example, metallic zinc has sufficient chemical energy to reduce either hydrogen or lead to the free state from certain combinations. This reduction of hydrogen and lead may take place simultaneously in juxtaposition, or separately, depending entirely on the conditions and the accessibility of the two substances to the reducing action. But the fact that hydrogen and lead may both be reduced together by the zinc, is no proof that the hydrogen reduces the lead or that the lead reduces the hydrogen. Therefore, instead of jumping at the conclusion that in such a reaction the hydrogen is reduced by the zinc, and that the reduced hydrogen, by a *subsequently simultaneous* reaction reduces the lead, it would have been more in accordance with scientific procedure to ascertain experimentally whether "nascent hydrogen" of itself, without the assistance of a more powerful reducing agent, is really capable of reducing the lead, or whether the lead is reduced only when the nascent hydrogen is produced by a reducing agent, which is itself also capable of reducing lead.

Fortunately there are many ways of producing nascent hydrogen. All hydrogen, as it is set free from combination, is, of course, nascent by definition, whatever may be the method of its production. This fact affords ample experimental means of determining whether nascent hydrogen has the power of reducing lead or any other substance.

If it is true that nascent hydrogen, produced by the dissolving of zinc in an acid, is capable of reducing lead salts to metallic lead, it must also be true that nascent hydrogen evolved by the dissolving of any other metal, or nascent hydrogen evolved electrolytically or by any other method, will also reduce lead. If there is such a thing as nascent hydrogen, having distinctive properties and powers, those properties and powers must be distinctive and must be the same in all nascent hydrogen, from whatever origin the hydrogen may have been derived. It has never been supposed that the nascent hydrogen originating from one source has one set of properties, and that originating from another source has another set of properties. Otherwise these peculiar properties could not appertain to the nascent hydrogen, but must belong to the various sources of the hydrogen, and there would be as many sets of properties as there are possible sources of hydrogen. There would, in fact, be many more. Electrochemical action is one source of hydrogen, and with the hydrogen so evolved there may be a simultaneous reduction of lead, zinc, or other metals, or there may be no reduction of a metal, depending altogether on the electromotive force maintaining the electric current.

Hydrogen, and therefore, nascent hydrogen, is easily generated on the surface of a sheet of zinc immersed in dilute HCl. If a strip of copper be attached to the zinc and both metals immersed in the acid, the nascent hydrogen will be generated in still greater quantities and most of it will be formed at the surface of the copper. The hydrogen formed at the copper plate is, in this case, reduced electrochemically, the arrangement constituting a short-circuited galvanic or electrogenic cell, of which the copper plate is the cathode and the zinc plate, the anode. If we introduce a salt of lead into the solution in contact with the copper cathode, metallic lead will be deposited on the cathode and the quantity of hydrogen liberated will be diminished. If a sufficient quantity of a very strong solution of the lead salt has been introduced in contact with the cathode, the deposition of lead will be very rapid and the quantity of hydrogen liberated may become so small as to be invisible. It was undoubtedly this phenomenon, the apparent substitution of reduced metal for the reduced or nascent hydrogen, which led to the assumption that the nascent hydrogen causes the reduction of the metal.

If, however, we prepare a second apparatus, identical with the

first in all respects, except that a mass of finely divided metallic tin is used instead of the metallic zinc, we obtain exactly the same result as far as the evolution of hydrogen on the cathode is concerned. The nascent hydrogen is generated in both cases and is produced in the same manner, in the same solution, and on cathodes of the same metal. But when we introduce the same lead salt in contact with the cathodes in the two apparatuses, we get very different results in the two cases. In the apparatus in which zinc is used as the source of the energy of the electric current there is a copious deposition of spongy lead and a great diminution in the quantity of hydrogen evolved. But in the apparatus in which tin is used as the source of energy of the electric current there is no deposition of a trace of lead, the formation of hydrogen (and, therefore, of nascent hydrogen) continuing at the cathode in contact with the introduced lead salt, exactly the same as before the introduction of the lead salt. If it is the nascent hydrogen in the one case that reduces metallic lead, why does not the nascent hydrogen reduce lead in both cases? The only difference in the condition of the two cases is a difference in the electromotive force of the reducing current.

The conclusion is unavoidable that the reduction of metallic lead at the cathode in the one case is not due to the nascent hydrogen, nor to any other hydrogen, but to the higher electromotive force of the electric current, which is maintained by the energy of the dissolving zinc and which is much greater than that obtainable from tin. These results cannot be accounted for on any supposition that hydrogen is the reducing agent. But without such an assumption the facts are all easily accounted for. The electrogenic power of zinc is greater than that of either lead or hydrogen and, hence, the electric current in the zinc-cell reduces both lead and hydrogen simultaneously. But the electrogenic power of tin is not greater than that of lead, hence, metallic lead cannot be reduced by the electric current in a cell deriving its effective electromotive force from tin, and in this case there is no reduction of lead, although nascent hydrogen is formed in abundance. The evolution of hydrogen in both cases is due to the fact that the electrogenic power of either zinc or tin is greater than that of hydrogen.

The supposition that nascent hydrogen is first evolved by a reducing agent and that this nascent hydrogen *subsequently and*

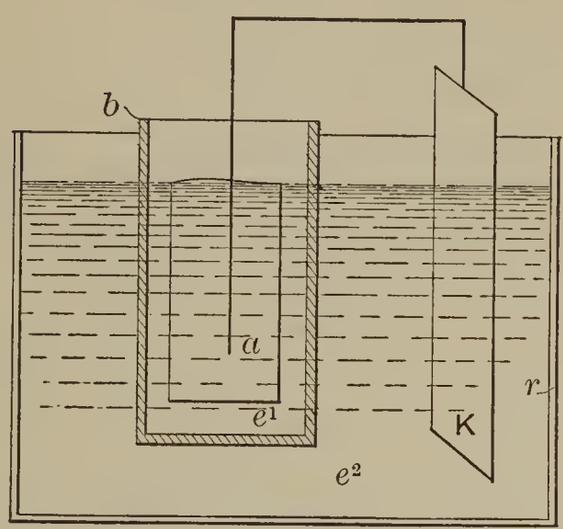
simultaneously reduces another substance cannot be supported, even theoretically, without ignoring thermochemical considerations. Hydrogen, whether nascent or ordinary, cannot reduce another substance, unless its chemical energy is greater than that of the other substance. But in that case the other substance would be reduced in preference to the hydrogen by the original reducing agent. The frequent reduction and liberation of hydrogen along with other substances is evidently a coincidence due to the fact that water or some other easily reducible compound of hydrogen is present in those cases and equally accessible to the reducing agent.

When the reducing agent is an electric current, as in the zinc cell above mentioned, it is easy to understand why the addition of the lead salt and the subsequent deposition of metallic lead causes the evolution of hydrogen to diminish or cease altogether. A cell of this type of fixed dimensions and form will have a certain resistance, which will not be greatly altered by adding the lead salt. The current which the anode in this cell is capable of maintaining on short-circuit will, therefore, be substantially the same whether the lead salt is present or not. Hence, the greater the quantity of lead deposited per unit of time, the less will be the quantity of hydrogen, since the total reduction must correspond with the total current according to Faraday's law of electrochemical equivalents.

A careful examination of the facts connected with this class of reductions shows that there is no experimental evidence to prove that nascent hydrogen is different from hydrogen in its ordinary state.

There are two general cases to be considered. In one case the substance supposed to be reduced by nascent hydrogen has greater chemical energy or reducing power than that of hydrogen itself; or, speaking electrochemically, the substance reduced is electropositive to hydrogen. Among the substances of this class that have been supposed at one time or another by various philosophers to have been reduced by nascent hydrogen, are the alkali and alkaline earth metals, also zinc, magnesium, aluminum, cadmium, lead, manganese and iron. But each of these metals is itself capable of liberating nascent hydrogen from aqueous solutions and it can be shown experimentally in the manner described above for lead, that nascent hydrogen, unassisted by a more powerful reducing agent, cannot reduce any of these metals.

The most convenient form of apparatus for these demonstrations is shown in the accompanying figure, and is familiar to us all as the "single-cell" electro-deposition apparatus. The anode *a*, is enclosed in a porous cup, *b*, in which is a suitable solvent elec-



trolyte, e^1. A second electrolyte, e^2, surrounds the porous cup and is contained in a suitable receptacle, *r*. The circuit is completed by immersing a copper or gold plate, *k*, into the electrolyte e^2, and electrically connecting it with *a*. If platinum is used it soon becomes almost a non-conductor, through some specific action of hydrogen.

The external electrolyte e^2, may contain any or all of the metals, K, Na, Ba, Ca, Sr, Mg, Al, Zn, Cd, Pb, Fe, Co, Ni, Mn and some others. The inner electrolyte, e^1, consists of dilute HCl and the anode, *a*, consists of spongy metallic tin, connected by a tin or platinum conductor to the cathode, *k*.

In the usual form of this galvanic cell Zn is used instead of Sn for the anode; but, as explained above, Zn gives an electromotive force high enough to reduce not only hydrogen, but also Pb, Cd, Sn, and Fe. In order, therefore, to obtain nascent hydrogen without using a reagent that we know will simultaneously reduce metals having greater chemical energy than hydrogen, we must employ as our anode, that is, as our source of electromotive force, the metal which stands between hydrogen and all others of higher chemical energy, namely, tin. With such an apparatus there is no difficulty in evolving nascent hydrogen abundantly on the plate *k*, in contact with any compound of any of the metals mentioned above, without the slightest reduction of anything but hydrogen and tin.

This seems to show conclusively that the reduction of these metals, when it occurs in conjuction with the evolution of hydrogen, is not caused by the nascent hydrogen, but by the same agent, which simultaneously reduces the hydrogen and which is of higher electromotive force than that necessary to liberate hydrogen. This is still more forcibly shown by the fact that an anode of lead will cause metallic Sn to be deposited along with the hydrogen; an anode of cadmium will cause Pb, Sn and H to be deposited; an anode of zinc will cause Cd, Pb, Fe, Sn and H to be deposited, while an anode of sodium or potassium will cause Zn, Cd, Pb, Fe, Sn, and H to be deposited.

For the deposition of H without the simultaneous reduction of Sn in the presence of a salt of Sn, certain particular conditions are required, owing to the facility with which metallic tin deposits metallic tin from a solution of a tin salt of different concentration. For this purpose we may use H_2SO_4 instead of HCl for the electrolyte, e^1, and $SnSO_4$ in the electrolyte, e^2. This deposits H without tin on a fresh Pt cathode. Or we may dispense with the porous cup and use a single electrolyte consisting of a uniform mixture of HCl and $SnCl_2$ in any convenient proportions. This is probably the best arrangement for evolving H in contact with a tin salt, as no tin is deposited, though H is abundantly evolved. I have found it more satisfactory to use an anode of spongy lead in dilute H_2SO_4 for generating the H in contact with salts of all other metals except tin.

The apparatus shown above may be modified by using two porous cups and a third intermediate electrolyte, wherever it may be necessary to prevent the formation of insoluble precipitates.

I have found by means of this apparatus that nascent H is unable to reduce even so powerful an oxidizing agent as PbO_2 in contact with H_2SO_4.

The second general case to be considered is that in which nascent H is supposed to reduce substances having less chemical energy, such as the compounds of Cu, Au, Hg, Ag, Pt, As, Sb, also HIO_3, HNO_3, and other powerful oxidizing agents.

For this purpose we may employ a similar apparatus, using as the anode a metal of lower chemical energy than H. But I have found it more convenient and satisfactory to electrolyze such compounds between platinum electrodes, using a current

from a source of electrical energy having lower electromotive force than that required to decompose water or liberate H. For this purpose the Zn-Hg or Latimer-Clark cell is well adapted, its electromotive force being slightly less than that required for decomposing water and ordinary acids. This cell deposits As from arsenious compounds, the platinum anode being surrounded by arsenic acid; Sb from $SbCl_3$, the anode being surrounded by $SbCl_5$; and Bi from $BiCl_3$. In all cases no hydrogen is or can be evolved, though oxygen is evolved at the anode. A necessary precaution, in order to prevent the possibility of any hydrogen being evolved, is to saturate the platinum anode electrolytically with oxygen. Otherwise the combination of the platinum with oxygen makes the evolution of hydrogen with the Clark cell possible at the beginning of the operation.

By using other sources of electromotive force of lower intensity, I have found that, with the liberation of oxygen at the anode, Sb may be deposited with less than 0.94 volt from $SbCl_3$; As, from $AsCl_3$, with 1.30 volts; Bi, from $BiCl_3$ with 1.24 volts; and I, from HIO_3 with 0.8 volt. The decomposition of HIO_3 by electrolysis has often been cited as an illustration of the reducing action of nascent hydrogen. But it is evident that there can be no hydrogen, nascent or ordinary, generated at the cathode in conjunction with free oxygen at the anode, unless the effective electromotive force is at least 1.48 volts, which is required for this separation. If it is claimed that the energy required for separation is simultaneously restored to the circuit by the recombination of the hydrogen, this claim amounts to the assertion that the hydrogen really plays no part in the reaction so far as the energy is concerned, and is an admission that the result, both as regards energy and matter, is exactly the same as though no hydrogen were present, the nascent power being merely the energy derived from the electric current.

Dr. Lothar Meyer in speaking of this subject in his "Modern Theories of Chemistry," says: "These secondary actions have not of necessity any connection with the passage of electricity, and perhaps have nothing to do with it. They obey the ordinary law of chemical reaction and are merely characterized by the fact that the ions are in *statu nascendi* and are consequently in a position to act very energetically." Continuing he says: "Iodic acid, HIO_3, or $H_2I_2O_6$, offers one of the most remarkable instances of

the case in point. . . . . The separation of iodine at the cathode is merely due to the secondary action of the hydrogen, $5H_2 + H_2I_2O_6 = I_2 + 6H_2O$."

According to this equation the hydrogen is exercising only its ordinary reducing power, which it has in its free state, that is, its energy of combination. But if this is nascent hydrogen, it must, while it is supplying this energy, be simultaneously absorbing the same quantity of energy from the source, which is supposed to be generating the nascent hydrogen. If this be so, hydrogen is really not exercising any power except that of receiving electrical energy or an electric charge from one ion and simultaneously transmitting it totally to another ion, which second ion is liberated at the cathode instead of the hydrogen. If this is the function of nascent hydrogen, it is what is ordinarily called conducting electricity and its action is no different at the cathode, where nascent hydrogen is supposed to be, from the action it may be supposed to exercise in any part of the electrolyte or from the action of any other ion in the body of the electrolyte. If this is what is meant by nascent hydrogen, it is evident that its powers are merely the power of acting as a medium of transmission for the electric current, like any other hydrogen in combination.

But this is evidently not what is meant by "nascent hydrogen" as the term is used by Dr. Meyer and by chemists in general. He speaks of the hydrogen in the equation cited by him for iodic acid as being "*in a position to act very energetically*," and his equation shows that the nascent hydrogen he means, is hydrogen which has been released from combination and which is capable of combining with oxygen to produce water and of simultaneously reducing iodic acid. But to produce such hydrogen under the condition cited requires 1.48 volts of effective electromotive force, while the electrolysis of HIO_3 requires less than 0.8 volt. Hence, the reducing agent is, as in the other cases, the electric current and not the nascent hydrogen.

The same reasoning and similar experimental facts apply with equal force to nascent oxygen and all other alleged nascent bodies. The only logical conclusion is that there is no argument in the mysterious *status nascendi*, which can add anything to the validity of any chemical or electrochemical theory.

DISCUSSION.

Mr. Henry S. Blackmore: Mr. Chairman, I would like to offer a little suggestion in regard to the reference advanced that the nascent state is shrouded in mystery, by its possible relation to another condition which is likewise shrouded in mystery, *viz.*, catalytic action.

The catalytic action of, for example, porous or spongy platinum on hydrogen and oxygen in the formation of water or sulphur dioxide, and oxygen in the formation of sulphuric anhydride is assumed to be a condition in which the gases are condensed by action of the contact substance with abstraction or liberation of energy until they are brought within the scope of their mutual attractions, combinations or reactions.

Now take in the case of the nascent state, for example, the result of the dissociation of water by electrolysis with the liberation of hydrogen at the cathode and oxygen at the anode. The liberated hydrogen we might assume, in its nascent condition, has not yet resumed its normal volume under ordinary atmospheric conditions and temperature, consequently in its nascent or condensed condition it might be in a similar form within the scope of its mutual attraction, combination, or reaction with relation to union or combination with associated substances to that produced by reverse or catalytic action in the condensation of gases. That is to say, the catalytic action deals with a condensation to a point within the scope of the mutual attraction of the associated substances, while the nascent state resulting from the dissociation or decomposition of compounds utilizes the same condition within the scope of the mutual attractions of the liberated substances before they have assumed their normal volume or conditions under ordinary atmospheric pressure and temperature.

In other words we might assume the nascent state to be the same condition under which ordinarily inactive substances unite within the scope of their mutual attraction as is produced by catalytic action, the one a condition produced by condensation and abstraction of energy, and the other a condition existing prior to expansion or resumption of normal conditions which nascent condition has been produced by application of energy.

I offer this only as a suggestion as to the possible relation be-

tween a possible like condition existing during the formation of compounds by catalysis and the nascent state, which condition is induced by opposite means, *viz.*, the abstraction of energy in one case and the addition of energy in the other.

Dr. C. A. Doremus: Mr. Chairman, there are hundreds of chemical reactions which do not involve, apparently, any electrolytic conditions, which are not capable of being brought about by hydrogen in a gaseous state, unless we influence that hydrogen by either heat or cause it to be evolved in contact—in intimate contact, with the substance to be acted upon. We are, all of us, familiar with the Marsh test, and ordinary hydrogen in the gaseous state will not produce it.

Since acetylene was produced in commercial quantities, various attempts have been made to convert it into ethylene gas. Acetylene, it was supposed, could be easily formed and have two hydrogen atoms added to it and made to C_2H_4. It was found, in the gas business, that acetylene did not increase the light-giving power of gas in proportion to the cost of acetylene; whereas, if it could be converted into ethylene it could be converted into something having light-giving powers. Various experiments were tried to cause the hydrogen to unite. One of the most recent of these was by the action of water on a mass which results from the fusion of calcium carbide with barium silicide. When these two substances are powdered and mixed together and thrown into water, the one generates acetylene and the other hydrogen, but practically no ethylene is formed. When, however, the two products are fused together and the fused mass then thrown into the water, as much as fourteen per cent. of ethylene is formed. We certainly have no electrolytic action there. And the conditions are such that the hydrogen is capable of uniting with the acetylene to produce this new additive compound. We now know that under this influence we have been able to get combination between gases that could not be obtained under ordinary conditions.

It seems, therefore, that from a chemical standpoint alone the condition of affairs have not changed. The words *status nascendi* have been very appropriate: it is in the process of the formation of some things that other chemical reactions take place. We are beginning to understand how complicated our chemical reactions are. In the well-known experiment of heating a mixture of manganese

dioxide with potassium chlorate, causing the evolution of oxygen at exceedingly low temperatures, it has been shown that there are several chemical transformations that take place simultaneously. We have been accustomed to look at only the end products—the oxygen and the potassium chloride—and to suppose the manganese dioxide undergoes no change. Such a view does not accord with the facts. In the production of the various compounds, as with the benzene derivatives, a number of compounds are produced simultaneously, and, unless these be considered, the cause of some chemical actions has been missed. We must assume, I think, if the molecules of elementary substances, such as hydrogen or nitrogen or oxygen, are complex—the molecules of compounds that are also complex in the process of breaking down—either the atoms or the radicals react under conditions which, for want of a better term or better explanation at present, we have to designate as that of *status nascendi.*

Dr. N. S. Keith: In the electrolysis of a copper solution, using an insoluble anode and a proper density of current, oxygen is freed at the anode, and there is a deposition of copper at the cathode, without any free hydrogen appearing. Now, if we go back to the use of the older formula and assume that sulphate of copper has the composition $CuO + SO_3$, then we might understand that oxygen will be set free from its associated copper by electrolytic action, and the sulphuric anhydride will absorb water and become sulphuric acid. Under the more modern chemical formula for sulphate of copper, oxygen from the water of the solution is set free, and its equivalent of hydrogen acts in its nascent condition at the cathode, it reacting to precipitate or deposit metallic copper upon it.

Dr. W. D. Bancroft: Mr. Chairman, it seems to me that Dr. Doremus struck the right note when he said that a great many of our reactions are nothing like as simple as we think them to be. Take a couple of cases for examples. If you electrolyze nitrobenzene with a platinum cathode, you get no aniline. If you use a zinc cathode you get some aniline. Now that has been accounted for on the ground that we need a higher electromotive force with a zinc cathode than with a platinum cathode. But, apply that, for instance, to the reduction of nitrates; with a zinc or iron cathode there is approximately the same amount of reduc-

tion, and a very much greater reduction than with a platinum cathode. Of course, the first suggestion is, you can replace the zinc by an iron cathode; but take the reduction of a chlorate and you find that there is much more reduction with an iron cathode than with a zinc cathode. To say that there is a specific action for each cathode in each solution is merely a confession of ignorance. The essential point is that we have, so far, no generalization which holds right through. Each case contains special features which distinguish it from every other case and matters are not as simple as Mr. Reed's paper might seem to imply.

President Richards: With the permission of Mr. Reed, I would like to make a remark in the line of the discussion, and that is, in starting, in regard to sulphuric acid acting upon zinc. We have there a liberation of energy; the solution gets warm. That heat which appears is a surplus of energy of the reaction which accompanies the evolution of the hydrogen. Is it not then true that in all cases where hydrogen is evolved, it is evolved accompanied by an excess of liberated energy? Now, I think with Professor Doremus that the term *status nascendi* has been used as a convenient term to cover the action of the agents which are evolved with the simultaneous production of energy and which in that condition produce effects which they do not produce when used alone. We have translated that term into the language of the atomic theory and said that the *status nascendi* is the state in which the atoms are alone or out of combination, as distinguished from their being in combination in the usual state. We can, however, put that in a different way, independent of the atomic theory, and simply say that the known actions of substances in the act of being liberated are due to the action of the substances plus simultaneously-liberated energy. When we take the case of sulphuric acid acting upon a piece of zinc we get H_2SO_4 equals H_2 plus energy. That energy appears, in the case of the solution of zinc in the sulphuric acid as heat. But we must not get away from the fact that we have hydrogen plus some energy, and hydrogen thus energized, in whatever form that energy may be, is more effective than hydrogen not energized; and whether we translate it into terms of the atomic theory and call it hydrogen in a nascent state or simply say energized hydrogen, it matters very little. Or we may take it in more general terms and say that substances in

the nascent state have more effective powers because of the simultaneously-liberated energy they possess: I would prefer to take the non-committal position.

Dr. C. A. Doremus: Mr. Chairman, I would like to point out in this case that we have, just as I explained, a series of reactions, because if we have hydrogen plus energy acting upon sulphuric acid, we get an action in which free hydrogen will not be produced for we get $8H + H_2SO_4 = H_2S + 4H_2O$.

You have given me the means of illustrating exactly what I wish to put before the meeting.

Mr. C. J. Reed: I will try to answer the objections of Dr. Richards and Dr. Doremus together.

I think if we assume for the sake of argument that the statement of Dr. Richards is correct, and that the energy which is liberated as heat in a thermochemical reaction can be utilized in *subsequently simultaneous* reactions, it must, nevertheless, be admitted, that the only available energy which the hydrogen possesses, is what is imparted to it by the reducing agent. It can have no energy except what it has received. It was previously in a combined state and had no available energy. If, in its liberation, the energy required for liberation and additional energy is given to the hydrogen, and if, in exercising its nascent power, it gives up all of this energy, it is only giving up what it received. In other words, it is only acting as the medium of transmission, as stated in the paper.

But I do not admit the supposition that energy, liberated as heat in the reduction of hydrogen in thermochemical reactions can be subsequently simultaneously utilized by the hydrogen as a part of its chemical energy in addition to the chemical energy it necessarily possesses. I am unable to see on what theoretical grounds such a supposition can rest. It seems to me that any energy which is liberated as heat in an exothermic reaction must necessarily disappear as heat. How can such heat be restored as chemical or electrical energy without a subsequent transformation?

In regard to the arguments of Dr. Doremus and Dr. Bancroft, they seem to have forgotten the point emphasized in the paper, namely, that in all those cases of alleged nascent activity, no hydrogen can be obtained for the purpose of reduction without the presence at the very same point of a more powerful reducing

agent, such for instance, as the iron filings or the zinc referred to. The fact that ordinary gaseous hydrogen alone, passing through arsenical reagents is unable, as Dr. Doremus says, to perform the reduction (in the March test), shows conclusively that such reductions are not caused by the hydrogen, but by the reducing agent which simultaneously reduces hydrogen. You ask why it is that we get H_3As when we dissolve zinc in acids in the presence of an arsenical compound, and do not get it by passing hydrogen gas through an arsenical solution? It is evidently because the zinc is a reducing agent capable of acting simultaneously upon the hydrogen compound (the acid) and upon the arsenical compound, while hydrogen is incapable of reacting on either the acid or the arsenical compound. We have in the March test a number of reagents acting together, the zinc, the arsenical compound and a compound of hydrogen. Why is not hydrogen like any other chemical element? Why can it not go out of one combination and into another in the presence of a reducing agent without our assuming it to be the reducing agent? Could we not with equal reason assume that the arsenic instead of the hydrogen is reduced by the zinc and that this arsenic is the nascent substance, which, by a subsequently-simultaneous reaction, combines with the hydrogen? Would not this be the more reasonable supposition, since arsenic is more easily reduced than hydrogen? Zinc reduces the arsenic from an arsenical compound, if no acid is present, and reduces hydrogen from an acid, if no arsenical compound is present. When both are present why should it not produce H_3As, a compound of both of the products liberated by the zinc? Why must we suppose that one reaction precedes the other, when we know that each is independent of the other? It is no uncommon thing to combine two reactions, in order to get a compound of what would otherwise be separate elements. We may, for instance, by heating certain peroxides, obtain free oxygen and a lower oxide, and by heating certain higher sulphides, obtain free sulphur and a lower sulphide; while by heating the higher oxides and sulphides together we obtain sulphates. And such reactions usually occur with explosive violence. Yet we never speak of them as being caused by nascent sulphur, or nascent oxygen. This is precisely the case when water acts upon calcium carbide and barium silicide. If the two solids are acted upon separately by the water, one

generates acetylene and the other hydrogen; but if the two solids are previously fused together, so as to bring the two reactions within molecular distances, the products, hydrogen and acetylene combine and form ethylene, exactly as the reduced hydrogen and reduced arsenic in the March test combine to produce H_3As. But when coarse lumps or even powdered calcium carbide and barium silicide are mixed together and treated with water, there is, as Dr. Doremus says, "practically no ethylene" formed, because the reactions are practically in separate localities. Even the fusion together of the two solids produces, as is admitted, only "as much as fourteen per cent. of ethylene." What evidence have we that the mere fusing together of the carbide and the silicide causes either the hydrogen or the acetylene to become nascent?

Why must we suppose that hydrogen acts in some peculiar, unexplained way and that it has a special monopoly of energy? We know in these cases cited it is always the metallic zinc, iron, carbide, or silicide which gives up the energy. The hydrogen is in combination before and after the reaction, and has no available energy before or after. What evidence have we that it possessed other available energy in any intermediate state? No illustration can be mentioned in which hydrogen has any nascent or reducing power, except those in which the hydrogen is generated at the point of reduction by a greater reducing power than hydrogen itself, acting at the same point.

Dr. Bancroft, I think it was, gave another illustration of the reduction of nitro-benzene to aniline. The electric current alone produced very little aniline, though it evolved hydrogen, while metallic zinc caused much greater reduction. It does not require as high an electromotive force to reduce hydrogen as that which can be produced by zinc. How do we know it is not the zinc or a current of higher electromotive force produced by zinc in this case that is the reducing agent? There is less reduction with a small current evolving hydrogen than with zinc. This shows that zinc is a more efficient reducing agent in this case than either hydrogen or the small electric current.

Why is it that the nascent hydrogen formed in a solution of nitrate or chloride of lead, in the manner I have described, will not reduce any lead on a platinum plate, if the source of the hydrogen is tin, whereas, if the source of the hydrogen is zinc, we get a

copious deposition of lead? There is the same kind of nascent hydrogen in both cases. In one there is reduction, in the other, there is not. This seems to me to show conclusively that the zinc, or an electric current produced by the zinc, is the reducing agent, and not the hydrogen.

In regard to the deposition of metallic copper, as spoken of by Dr. Keith, the reaction which he mentions takes place at a less electromotive force than that which is required to reduce hydrogen. That case comes under the second class of compounds to which I referred.

There seems to me no evidence of a nascent state in the reduction of nitrates and chlorates with cathodes of various metals such as iron, zinc and platinum. Dr. Bancroft will doubtless admit that the quantity of nitrate or chlorate reduced by electrochemical action will depend upon the quantity of electricity only and not upon the composition of the electrode. This was experimentally demonstrated by Faraday in a manner so complete as to be hardly questionable now. If there is a greater reduction of nitrate with the zinc or iron cathode than with the platinum cathode, that additional reduction is clearly due to a separate chemical action between the metallic zinc or metallic iron and the nitrate and that reduction would take place with no current passing. If there is a greater reduction of chlorate with an iron cathode than with a zinc cathode, this additional reduction is also clearly due to the action of metallic iron on the chlorate, or possibly, to the action of a ferrous salt, which has formed, upon additional chlorate.

President Richards: I am sure that this discussion could be prolonged with profit and interest to all of us, but on account of the exigencies of the program, the Chair shall have to declare the discussion closed.

A paper read at the Inaugural Meeting of the American Electrochemical Society, Philadelphia, April 4, 1902, President Richards in the Chair.

THE ELECTRICAL REDUCTION OF LEAD.

By Pedro G. Salom.

It has been almost universally accepted by electrochemists, that when a reducing action takes place at the cathode of an electrolytic couple, that this action is due to the nascent electropositive substance produced by electrolysis. I myself held this view, until comparatively a short time ago, when I was forced to the conclusion that a more satisfactory explanation would have to be found, and after hearing Mr. Reed's paper on the "Nascent State," it seems to me that his views on the subject make the matter entirely clear.

The reduction of lead, therefore, by my process, while it is clearly not an electrodeposition process, can no longer be properly described as a secondary result of electrolysis, since, if the hydrogen produced at the cathode is not the reducing agent, the reduction must be effected by the direct action of the current itself under the special conditions obtaining.

The process as now conducted at the works of the Electrical Lead Reduction Company, at Niagara Falls, is as follows: The ore, after having been carefully washed to remove as far as possible the dirt and loose gangue, is ground to a fine powder (about 40 or 50 mesh) and placed in cast antimonial-lead cells in the shape of truncated cones, about 2 feet in diameter at the top, and 15 inches on the bottom, and 6 inches high, with a flange on the outside, so arranged as to fit on the top of another cell. This enables us to stack them up 10 or 12 high, electrical connection being made through the electrolyte, the cells themselves being insulated from each other by a rubber lining entirely surrounding the inside wall of the cells, and spreading over the top, at the same time making a good seal to prevent the electrolytic gases from escaping into the room.

The cells are charged with about 12 pounds of ore, filled about two-thirds with dilute sulphuric acid, connected up in series of about 48 cells, and a current of about 1 ampere per pound is

turned on, requiring from 125 to 130 volts, or about 2.5 volts per cell, practically the same as a storage battery. At this current density the operation for complete reduction requires five days. A higher current density can be employed and the time shortened, but only at the expense of efficiency in the amount of power required per pound of ore, unless the size of the electrodes is increased proportionately to the increase of current.

Lead being a *dyad*, its electrical equivalent is 103.5, and consequently every coulomb or ampere second will produce a little over one milligram of lead,—hence, 454,000 ampere seconds or 126 ampere hours will produce 454 grams, or 1 pound,—126 ampere hours at 2.5 volts, equals 315 watt hours, or a little less than $^1/_2$ electrical H. P. hour per pound. In practice we find it requires a little more than this, although under proper conditions this figure need not be greatly exceeded. As a $^1/_2$ electrical H. P. hour at Niagara Falls, only costs $^1/_8$ of a cent (equivalent to $2.50 per ton of lead), the power required for reduction is not a serious item of expense.

After the ore has been subjected to the action of the current for five days, the cells are taken down, the acid poured off, the resulting mass of spongy lead scraped out, and a new charge of fresh ore put in, and the cycle starts over again. The sulphur originally contained in the ore passes off as sulphuretted hydrogen gas, which we propose to burn to sulphurous acid and convert into sulphuric acid. The sponge is then thoroughly washed to remove all the sulphuric acid, and can then be compressed into ingots of lead, or converted into the various compounds of lead direct. Owing to its spongy nature it is readily converted into litharge and white lead.

The operation for litharge requires about $1^1/_2$ or 2 hours, and for carbonate about 24 hours. At present we are confining ourselves exclusively to the manufacture of litharge, although it is manifestly the intention of the company to make all of the various compounds of lead.

Only one serious difficulty has been met with in carrying out the process on a commercial scale, and that is the question of incomplete and imperfect reductions,—the resulting sponge sometimes only analyzing 90 or 92 per cent. metallic lead. This difficulty has been overcome in the past by a subsequent treatment of the sponge, and now that we know the cause of the same, will be entirely eliminated in the future.

For the last six months of 1901, we manufactured and sold some 235,000 pounds of litharge, and are daily increasing the output.

Another difficulty we have had to encounter has been the action of the sulphuretted hydrogen on the eyes of the workmen. While it has no permanently injurious action on the eyes, it makes them very sore when the men are exposed to the gas for any great length of time. This difficulty will also be overcome by some slight modifications in the process, and in the near future I shall take pleasure in giving a more detailed account of our work at Niagara Falls.

DISCUSSION.

President Richards: I should have said, in introducing Mr. Salom—and as long as he has not said it himself, I will say it now—that this process is in operation at Niagara Falls at the Electrical Lead Reduction Company's place, on a considerable scale, and Mr. Salom's remarks are based on the industrial production of the sponge.

Mr. W. McA. Johnson: Mr. Chairman, I would like to ask Mr. Salom if he gets any sulphur along with the sponge.

Mr. Salom: Yes; sometimes.

Mr. Johnson: How far is the galena unchanged?

Mr. Salom: It varies. That is one of the provoking things about the whole matter—we can't get constant results under, apparently, the same conditions. One day we get 95 per cent., say, and the next day 92 per cent. And it is very hard to locate the difficulty, when results are not constant.

Mr. Johnson: That is very largely caused, I suppose, by the sulphur insulating the galena from the current?

Mr. Salom: No; we are not troubled, to any extent, by sulphur. I think the sulphur arises from the sulphate of iron that may be in the acid. You know, we take the raw ore and it contains more or less impurities to start with—some sulphide of iron and sulphide of zinc.

Mr. Johnson: I think you will find incomplete extraction has very largely to do with the formation of sulphur, which acts as

an electrochemical insulator. I think that is the result in the Marchesi process, which was tried some years ago, and it proved a failure for the reason they couldn't obtain complete extraction. That incomplete extraction is caused very largely by the sulphur, which prevents a current from going through the mass.

Mr. Salom: We don't find the sulphur distributed through the mass. The layer of sponge that forms is possibly two inches or more thick and the sulphur, if any, would be on top. And very often the ore that is not reduced is right against the cathode; the very bottom part of the ore. But there is no regularity or rule about it: it might be on top one time and down at the bottom at the next.

Mr. C. J. Reed: It seems to me that the difficulty experienced by Mr. Salom is very interesting proof that the reduction is not by nascent hydrogen. (Laughter.)

Mr. Salom: That is what I thought, after hearing your paper.

Mr Reed: It is very evident to me that the accumulation of reduced lead around the ore insulates, as Mr. Salom states, the particles of galena. They are thus removed from the sphere of electrochemical action, and consequently the current passes to the reduced metallic lead. Then the only possible chemical action is one evolving hydrogen, and consequently we get the most hydrogen after this occurs. In other words, the inefficiency increases towards the end of the process, and there will finally remain some particles of galena that are entirely insulated from the electrochemical action. If, however, the reduction of lead were caused by hydrogen, there would be no unreduced galena, as the hydrogen could penetrate into the smallest holes and reach the last traces of galena.

Dr. N. S. Keith: This process is a very interesting one, but the material (a pure galena) to which it is applicable is not so largely produced as is the other lead product, containing silver and gold, known as base bullion. This base bullion can be, as I showed some years before the time people thought that electricity could take much, if any, part in chemical work, refined, its silver and gold separated at a very low cost, and a spongy lead produced, perhaps not so spongy as this, because the deposit is simply crystals of lead. I carried on many experiments with such lead at that time, especially in the production of various materials which

have been shown here. One of the materials which could be produced, of an exceedingly high order, was carbonate, or white lead. The material produced under Mr. Salom's process does not promise as well, owing to the impurities in the galena, which would preclude the manufacture of the sponge lead, it seems to me, into white lead.

MR. C. HERING: Perhaps the reason why some of the sulphide is not reduced, is that the sulphide may act like the sulphate. I do not know what the heat of combination of the sulphide is, but the electromotive force for reducing the sulphate to spongy lead, is almost exactly that which is necessary to produce hydrogen on a plate of lead; hence a current will be very apt to do both or either one or the other, as the energy required is almost precisely the same. If the energy of combination of the sulphide of lead is equal to that of the sulphate of lead.

PRESIDENT RICHARDS: It is much less.

MR. HERING: Then the current ought to reduce the sulphide, and this therefore is not the explanation.

I would like to ask Mr. Salom how he gets rid of his gangue; the reduced sulphide must contain many of the other minerals which were in the original ore. I would also like to ask whether any attempt is made to refine the material and get out any valuable metals like silver.

MR. SALOM: The ores come chiefly from Joplin, Missouri, and I don't know whether they carry any silver or not; if they do, it is only a minute trace. I know it is not any considerable amount; certainly not enough for refining purposes.

In regard to the gangue, we get ore at our works without any difficulty, containing 80 per cent. and sometimes a little more, of metallic lead. The theoretical contents of pure galena are 86.61 per cent. of lead, and 13.39 per cent. of sulphur. So we only have 6 per cent. of gangue to start with. The ore is jigged, and we thereby remove practically all of it, except particles of gangue that are actually attached to the crystals of galena. The action—during reduction—has a tendency to bring the gangue to the surface. I don't know whether it is by the gas coming up through it, but a large part of the gangue is on the top of the reduced ore. Then the sponge itself, after it is taken out, is also washed on a washing trough before it goes to the litharge room

for drying and burning, which still further removes any unreduced ore or gangue.

One point I intend to emphasize is that owing to the spongy nature of the material, it is roasted or converted into litharge very much more rapidly than by the method of melting lead and exposing it to the air in a revolving tubular furnace, such as we saw at Harrison's yesterday. What we call good reductions average from 92 to 95 per cent., and we can readily roast the sponge in an hour or an hour and a half's time, to litharge. It might be in the furnace a little longer time than that, but the actual time for conversion at the hottest part of the furnace is not over an hour, I think. We have a long furnace, and the sponge is gradually brought along. It won't do to put the greatest heat on it at first.

Mr. E. A. Sperry: I would like to suggest perhaps the incomplete reduction is due to the initial and final density of the electrolyte. That might help to explain it.

Mr. Salom: That does not vary. It is not like using it up in a storage battery, by sulphating the plates.

Mr. Sperry: There is a using up of the water?

Mr. Salom: Oh, yes. We add water to the cells in order to keep the level at the same point; and the acid is maintained at about 10 per cent.

Mr. Reed: I would like to ask Mr. Salom whether he has ever tried sulphur dioxide to overcome the fumes of hydrogen sulphide. I mean injecting a little sulphur dioxide to convert whatever hydrogen sulphide there is into free sulphur.

Mr. Salom: That would be very difficult because all the gas is not in the top of the cell; it is adhering to the sponge. It is after the electrolyte is all poured off and when scraping out the sponge from the bottom of the cell, that most of the gas is liberated. So, unless we treat the whole mass to something of that kind, we would have the same difficulty.

A Member: What is done with the hydrogen sulphide gas evolved?

Mr. Salom: In connection with the utilization of sulphuretted hydrogen gas; we fully intend doing that, because we have not only sulphuretted hydrogen but we have hydrogen and oxygen in exact chemical proportions, and therefore the utilization of it in any kind of gas engine would be

an ideal condition. As I mentioned this morning, the fact is, we would get more energy than we put into the dynamo.

PRESIDENT RICHARDS: I will take just a brief moment to say something about the energy of the burning gases being more than the energy used by the dynamo in decomposing the ore. It is a fact, and is easily explainable without controverting the doctrine of the conservation of energy. The substances to be decomposed are PbS and H_2O. You have on the other hand, as the heat evolved, the heat of formation of H_2S. The dynamo must furnish the algebraic sum of these energies, that is, the heat absorbed minus that generated. When we burn the H_2S we have the formation of H_2O and SO_2. We have that much heat generated. The heat of formation of H_2O is equal to the heat absorbed in decomposing the water, so that factor is the same on both sides, and the heat of oxidation of sulphur to SO_2 is much greater than that required to decompose lead sulphide. It results that the combustion of the gases produces much more energy than is expended by the dynamo in producing them.

With regard to Mr. Johnson's remark comparing it to the Marchesi process, I think I should make a remark, because, that is rather a misconception of the process. This process is to use the lead sulphide as cathode and decompose it there by the reducing action at the cathode. The Marchesi process was to use copper sulphide as the anode, from which the copper was dissolved out by the acid set free there, leaving the sulphur behind; so that what has been referred to as a shunting of the current because of the liberated sulphur does not apply to the method of Mr. Salom. Nor do the remarks with regard to refining the metal apply, because refining takes away the metal and leaves the impurities, while Salom's method reduces the metal *in situ* leaving in it any impurities in the ore.

A paper read at the Inaugural Meeting of the American Electrochemical Society, Philadelphia, April 4, 1902, President Richards in the Chair.

ELECTROLYTIC REFINING OF COMPOSITE METALS.

By Titus Ulke, M.E.

The art of electrorefining composite metals, whose practical development represents the most advanced stage of applied metallurgy, relates to alloys of two or more metals, each of which is present in such quantities that it is an essential constituent of such alloy, as distinguished from merely impure, raw or crude metals, such as argentiferous copper, crude nickel and silver, or gold bullion.

The beginning of the art of electrorefining impure metals dates from 1865, when James Elkington's first English patent was granted, and his process applied in a little electrolytic plant near Pembrey. This method of refining has developed into an enormous industry, handling over three-quarters of the world's production of copper, and also a very considerable proportion of the silver and gold extracted annually.

The evolution of the art of electrorefining composite metals is of more recent date.

Perhaps the earliest attempt to electrodeposit, separately, more than one metal of an alloy or matte, in any continuous or semi-continuous process of refining such substances, was made by Emil André, who obtained a German patent, No. 6048 of November 1, in 1877. André's process refers chiefly to nickel-copper material, and consists, briefly, in suspending such material, cast into plates, as anodes in an acid solution, and electrolytically depositing out most of the copper on cathode plates of sheet copper, and finally the balance of the copper on such plates, with carbon anodes put in place of the nickel-copper anodes, this deposition occurring necessarily under varying and, therefore, in my opinion, commercially impracticable chemical and electrical conditions, then withdrawing the entire solution thus freed from copper, and recovering the nickel from the same, after removal of any iron it contains and making it ammoniacal by electrodeposition of the

nickel on suitable cathodes and with anodes of ordinary iron or zinc. This process was tried in Germany and abandoned.

The firm of Basse and Selve, whose nickel works are located near Altena, Germany, obtained a German patent dated December 22, 1891, for a process of double electrolysis and simultaneous separation of nickel, iron, cobalt and zinc, embracing essentially the following steps:

To the neutral or slightly acid solution of the salts of these metals is added a sufficient quantity of any organic substance, such as tartaric or citric acid, glycerine or dextrose, capable of preventing precipitation of the oxides of the above metals with alkalies, then adding concentrated caustic soda or potash in slight excess, and electrolyzing this alkaline solution.

At a current density of 0.3 to 1.0 ampere per square dcm., it is claimed that iron, cobalt and zinc are deposited on the cathode, while all or nearly all of the nickel remains in solution. The latter is now withdrawn and treated with sufficient ammonium carbonate to convert all of the free caustic into sodium or potassium carbonate, and the resulting solution electrolyzed to recover metallic nickel.

Prof. P. de P. Ricketts' U. S. patent No. 514,276 of February 6, 1894, relates to the electrolytic separation of nickel and copper, and covers a process consisting in the electrolysis of solutions of these metals, after having added alkaline sulphates to such solutions. While the copper is being deposited upon suitable cathodes, the nickel in the electrolyte is said to precipitate and collect in the bottoms of the electrolytic tanks, as double salts of nickel and alkali, which salts precipitate all the more readily out of the solution, the more acid the latter becomes.

The late Dr. Carl Hoepfner obtained a British patent, No. 11,307, accepted June 8, 1895, for treating nickel matte, by dissolving the metals contained therein by means of cupric chloride, which is said to dissolve the sulphurets and is itself thereby reduced to cuprous chloride. This solution of cuprous chloride is decomposed in a bath having a diaphragm between the electrodes, and its copper is deposited on the cathodes. The solution, from which all the copper has been taken out, is then freed from iron and from all those metals which are more negative than nickel or cobalt, and finally, the latter metals are precipitated either electrolytically or chemically.

Prof. Alexander Classen, of Aachen, Germany, separates copper from nickel by adding to the solution of these metals sufficient ammonium oxalate to form a double salt, and electrolyzing the heated solution, kept acid by addition of oxalic, tartaric or dilute nitric acid. The tension at the electrodes must be kept within the limits of 1 to 1.3 volts. After the deposition of all the copper, the nickel may be precipitated from the solution by neutralizing it, adding a slight excess of ammonium oxalate, and passing a current of at least 3 volts through the solution. Classen's process would be too expensive to work commercially, on account of the cost of the reagent and the cost of the platinum anodes employed therein.

In the *Engineering and Mining Journal* of January 30, 1897, page 114, I proposed the following method of separately and electrolytically recovering nickel and copper from bessemerized matte or nickel-copper alloys:

The essentially metallic material, containing both copper and nickel and also precious metals, is cast into anodes and suspended in a sulphuric acid solution of these metals opposite cathodes of sheet-copper, and electrolyzed as usual in copper refining, all the gold, silver and platinum originally in the anode plates being recovered in the anode residue or slimes and separately refined.

After the bulk of the copper has been electrodeposited out of the solution in the tanks, the remainder is completely recovered, in separate tanks, by adding just sufficient sodium sulphide to the withdrawn solution, rich in nickel, to precipitate out all of the copper, or by passing the solution through a filter of nickel sulphide, according to a suggestion of Dr. C. Whitehead, whereby the copper replaces the nickel and the latter goes into solution.

The filtered nickel solution is now free from copper, and after neutralization or being made ammoniacal, can be electrolyzed with anodes of graphite or gas-carbon, and the nickel deposited in thick sheets on cathodes of sheet nickel.

Last year, Dr. W. Borchers, of Aachen, Germany, proposed to treat ordinary nickel-copper matte like that produced near Sudbury, Canada, as follows:

The matte is enriched by smelting or converting, cast into anodes, suspended in an acid solution opposite suitable cathodes, and the bulk of the copper electrodeposited as usual; the electrolytic solution is then transferred to special tanks and the re-

mainder of the copper in it precipitated by scrap iron; the solution, now practically free from copper, but containing nickel and iron, is concentrated by evaporation, after the addition of ammonium sulphate, and the double salts of nickel and of iron are recovered separately, the former precipitating out at a concentration of the solution corresponding to 20° to 28° Baumé, while the latter does not crystallize out until a concentration of 30° Baumé is reached.

In this way a separation of the iron from the nickel is effected, and the latter may be recovered from the double salt of nickel and ammonia by electrolysis. This process, Dr. Borchers states, is about to be tested in Germany.

H. A. Frasch, of Hamilton, Canada, obtained several U. S. patents, during 1901 and 1902, relating to the electrolytic separation and recovery of nickel and copper.

As described in the *Engineering and Mining Journal* of September 8, 1900, and applied to copper-nickel matte, Frasch's process consists essentially in the electrolysis of a brine solution, so as to produce caustic soda solution in the cathode section of a divided electrolytic tank, and chlorine in the anode section, in which is placed the nickel-copper matte, the metals in the latter being dissolved and forming chlorides.

The copper in the solution thus obtained is recovered by electrodeposition, the nickel being separated from the cobalt, iron, and the remaining traces of copper as a double salt of nickel and ammonia, while the caustic alkali is recovered from the solution withdrawn from the cathode section as a by-product. The matte, coarsely crushed, is charged directly on a layer of carbonaceous material in the anode section of the tank, and is covered by a thin layer of sand, which is said to make a very satisfactory diaphragm for the separation of the resultant solutions of caustic soda and the chlorides of the metals. The tank is now filled with brine which is then electrolyzed, and the metallic solution obtained in the anode section and the alkaline solution in the cathode section are periodically displaced by fresh salt solution.

When it is decided that the nickel-copper matte on the bottom of the tank has received sufficient treatment to require removal of the solid residue, the upper layer of sand is taken out and washed for re-use, and the leached or partly leached material removed.

Hoepfners and Frasch's processes were both tried last year on

a small commercial scale at Hamilton, Canada, but have not yet attained practical prominence.

D. H. Browne, of Cleveland, Ohio, secured a Canadian patent, No. 74,401, of Jan. 14, 1902, being a reissue of patent No. 69,729, dated Dec. 21, 1900, and assigned to the Canadian Copper Co., consisting essentially in suspending anodes of the nickel-copper alloy in a solution of the chlorides of nickel and copper, electrodepositing the copper out of the latter on copper cathodes, circulating the solution through a shot tower containing broken or granulated pieces of the bessemerized matte or alloy to be treated, in contact with a salt solution and chlorine evolved in a later step of this process, so as to form additional cuprous and nickel chloride, and finally returning this solution to the copper depositing tanks. When the greater portion of the copper has been thus extracted, the solution, now rich in nickel but poor in copper and containing iron, is freed from the latter by ammonia and also from copper, although how this is to be actually done is not stated in the patent, and the chloride solution electrolyzed to obtain the metallic nickel, with carbon anodes contained in a water sealed compartment and suspended opposite sheet nickel cathodes, while the chlorine evolved is drawn off and passed to the shot tower for dissolving additional nickel and copper from the material that is treated.

I understand that this process has been employed for some time in a plant near Cleveland, Ohio, which is now producing from 8 to 15 tons of electrolytic nickel monthly.

Inspections of the principal electrolytic works here and abroad, and a close study of the above-described processes of refining composite metals convinced me of the fact that there was a radical defect in all of the above processes, in that they were not continuous enough, or not commercially practical enough, to successfully compete, for all purposes, with the well-established Orford separating process. This latter process is essentially mechanical in its nature and is based on a fluxing process which is comparatively cheap in operating cost, and is the only one at present employed in America for obtaining a large tonnage of nickel pure enough for use in making good nickel-steel and in casting good anodes for nickel-plating.

As the result of many experiments and investigations, I finally solved the problem of devising such a practical and continuous

electrolytic process and invented certain improvements in the art of refining composite metals, for which I obtained U. S. Letters Patent No. 694,699, dated March 4, 1902, and a Canadian patent No. 75,192, granted March 18th.

My invention is particularly designed to extract copper and nickel of commercial purity from nickeliferous copper material, although it applies generically to the electrolytic refining of nearly every alloy or bessemerized matte of two or more metals.

In refining nickeliferous-copper material the process consists in electrolytically depositing the copper from an acid solution of such material; periodically withdrawing a very small portion of the electrolyte as it becomes poorer in copper and richer in nickel; separating the copper and nickel salts contained in the withdrawn electrolyte; electrolytically depositing the nickel from a non-acid bath of the nickel salt with the use of an insoluble anode; periodically withdrawing and concentrating portions of the impoverished nickel-bath; and periodically restoring to the copper and nickel baths respectively the copper and nickel salts obtained from the withdrawn solutions.

In the electrolytic processes of refining composite metals and especially nickeliferous-copper material heretofore attempted or suggested, it was the invariable practice or attempt to dissolve the composite metals and use the complex solutions thus obtained as an electrolyte, and with one exception, to use an insoluble anode for depositing one of the metals—say the copper—so that the electrolyte eventually became so greatly impoverished in copper as to require a considerable increase of the electromotive force for further depositing the copper, and in order to extract all or nearly all of the copper, the electromotive force had to be increased to an inconvenient degree.

In this manner, and also in the case of the exception noted above, the conditions of depositing the copper varied theoretically from moment to moment and practically so frequently, as to require constant attention and readjustment of the electrical conditions to meet the varying chemical conditions. The next step in such old processes would then be to deposit the nickel under variable and therefore commercially impracticable chemical and electrical conditions, again by the use of an insoluble anode, and this carries with it the same inconveniences as the use of such anode in depositing the copper. In some cases, as we have seen, it has

been suggested to use a soluble anode, such as zinc, in the deposition of nickel; but this resulted of necessity in the contamination of the deposited nickel with zinc or other metal of the soluble anode.

By my improved process I avoid these inconveniences, and render the deposition of both the copper and the nickel practically uniform and continuous, notwithstanding the fact that for the electrolytic deposition of the nickel I also use an insoluble anode. The uniform continuity of my process is secured, in a measure, by utilizing in the deposition of the copper some of the material yielded in the extraction of the nickel, while the extraction of the nickel becomes uniformly continuous, by utilizing in the same some of the material rejected or withdrawn in the process of deposition of the copper. Thus in my process the depositions of the two metals are operatively connected and are in a manner dependent upon each other.

The uniform continuity of the refining process is secured not only with nickel-copper material, but with other composite metals when the same are composed of two metals, one of which yields a compact deposit from an acid solution with a relatively low voltage and current density and the other a like deposit from a non-acid solution with a relatively higher voltage and current density. The most important metals of the first order are copper and cadmium, and the most important metals of the second order are nickel, cobalt, and zinc. The composite metals, therefore, which may be treated with particular advantage by my refining process, are copper-nickel, copper-cobalt, copper-zinc, and cadmium-zinc; but the most important of these composite metals is nickeliferous copper material, and in the following I shall treat of this material specifically, with the understanding that in the more important steps of the refining process cadmium would be the equivalent of copper and either cobalt or zinc would be the equivalent of nickel.

While all nickeliferous materials can be treated by my process it is of advantage to employ a material that contains not more than 20 per cent. of nickel and not less than 80 per cent. of copper. Such nickel-copper material I cast into plates, suspend the latter as anodes in a suitably heated electrolyte—a solution of sulphate of copper and nickel or of the nickel-copper material and which contains free sulphuric acid—and I use sheets of copper as cathodes. By passing an electric current from the anodes to the

cathodes through the electrolyte, the anodes are gradually dissolved, and commercially pure copper is deposited upon the cathodes. The electrolyte is kept in circulation, as usual, in any well-known manner.

Since the anodes are not made of pure copper, the electrolyte, if not renewed, would soon become appreciably poorer in copper and richer in nickel. In order, therefore, to prevent or diminish undue enrichment in nickel and impoverishment in copper and in order to make the recovery of these metals commercially profitable, I regularly withdraw a certain amount of the solution for treatment in the manner which I shall describe further on. The amount of solution to be withdrawn at any one time should be such that the amount of nickel it contains is equal to the amount of nickel dissolved from the anode since the last withdrawal. Guided by this rule, the volume of the solution to be withdrawn periodically is readily computed. If, for example, the anode contains 10 per cent. and the electrolyte 4 to 5 per cent. of nickel, and the anode is completely dissolved in ten days, and if the total volume of solution in circulation is six times the volume of the electrolyte in the depositing-tanks, it is found that about 2.5 to 3 per cent. of the total volume of solution should be withdrawn daily. The amount of electrolyte thus withdrawn, is replaced by a sufficient amount of acid solution of copper sulphate, so as to re-establish the original condition of the electrolyte. A portion of the sulphate of copper needed for replenishing the electrolyte is obtained as a residue or by-product in the extraction of the nickel, as will appear further on. This withdrawal and replenishment would ordinarily be done periodically; but the periods may under some conditions be so frequent as to make the withdrawal of a portion of the electrolyte relatively poorer in copper and the replacement of it by an equal amount of normal solution practically continuous.

The next step in my process is the separation of the two metallic constituents from the withdrawn acid electrolyte, which, as stated, is impoverished in copper but rich in nickel. This may be done by any suitable method, for instance by precipitating the copper with hydrogen sulphide in a circular process, or by adding ammonia or ammonium sulphate obtained by the last step of my process, as will appear further on, to the heated solution, but still keeping the latter acid, and then cooling the solution.

In this manner the nickel salt is both precipitated and crystallized from the solution. The salt thus obtained will contain a small percentage of copper, and in order to remove all copper, it is again dissolved and the process of precipitation and crystallization is repeated until the nickel salt is obtained practically free from copper. The copper contained in the mother-liquor is used for replacing in part the copper deposited from the original electrolyte. The nickel salt obtained may be sold as an article of trade for any purpose whatsoever, but I prefer to continue the process for the extraction of the nickel.

If the nickel salt is obtained as I have just described, it is dissolved in water and sufficient ammonia is added to make the solution ammoniacal. If the nickel salt is obtained as in the first-mentioned separating process, already in solution, this solution is likewise made ammoniacal. The ammoniacal-nickel-salt solution constitutes the electrolyte for the electrolytic deposition of the nickel. It is preferable used hot.

In depositing the nickel I preferably use anode-plates of lead or of passive iron, and cathode-plates of any suitable material, but preferably one having a nickel surface.

The use of lead as the material for the anodes would at first glance seem to be impracticable, because of the formation in the process of electrolysis of sulphate and peroxide of lead on the surface of the anode, which former compound is soluble in ammonium sulphate. It would thus seem that the anode would gradually be consumed by sulphatization and solution, and that the deposited nickel would become so impure by co-deposited lead as to be of little value. I have found, however, that this is not the case. I have found that the lead anode remains practically intact and that only a very small amount of lead goes into solution and is deposited with the nickel, and even this can be removed in casting. The nickel obtained in this manner is, I believe, purer than any brand of nickel now on the market.

As the nickel electrolyte would eventually become impoverished in nickel unless this metal is replaced in the solution, and in order to prevent the saturation of the solution with ammonium sulphate, I periodically withdraw a portion of the electrolyte from the nickel-depositing system and recover the contained nickel salt and the ammonium sulphate or ammonia, the latter being used to make the regular nickel electrolyte ammoniacal. Nickel sulphate

obtained from both the solution withdrawn from the copper-depositing system and the nickel-depositing system is added to the regular nickel electrolyte periodically to replace the nickel deposited from the latter and to keep the solution of normal strength.

In conclusion, I will state that the tests which I have so far been able to make indicate that in commercial application, upon a large scale, my process will yield a nickel of greater purity at a smaller cost, than by any of the processes heretofore used upon a commercial scale.

A paper read at the Inaugural Meeting of the American Electrochemical Society, Philadelphia, April 4, 1902, President Richards in the Chair.

A NOVEL CONCENTRATION CELL.

By Professor Henry S. Carhart.

If any excuse were needed for bringing before this Society a subject having no probable applications in the arts, it might be found in the immense stimulus which the theories of ionization, osmotic pressure, and solution pressure have given to the study of electrochemistry. Any fact affecting these theories, either as a support or a refutation, is worthy of consideration. Such a fact I have lately discovered. It does not appear in the literature of electrochemistry and does not conform to accepted theories.

Helmholtz's famous equation for the electromotive force of a voltaic cell will be readily recalled. It may be written as follows:

$$E = E_c + T\frac{dE}{dT},$$

where E is the electromotive force of the cell, E_c the electromotive force due to the chemical reactions, and T the absolute temperature. The fraction dE/dT is the temperature coefficient of the cell. If this coefficient is positive, the energy given out by the cell is in excess of the chemical energy transformed. The cell then takes energy in the form of heat from the surroundings and converts it into the energy of an electric current.

If in the Helmholtz equation E_c is zero, that is, if no chemical energy is transformed, then the equation becomes characteristic of a concentration cell in which the electromotive force is proportional to the absolute temperature and the energy given out electrically is of purely thermal origin. The electromotive force of such a cell is therefore a resultant thermo-electromotive force, however it may be accounted for.

In a concentration cell of the first class the two electrodes of the same metal are immersed in a solution of a salt of this metal, the concentrations about the two electrodes being different. A familiar example of such a cell is the following:

$$Zn \mid ZnSO_4 \text{ (dilute)} \mid ZnSO_4 \text{ (concentrated)} \mid Zn.$$

The direction of the current through the cell is shown by the arrow, and the action of the cell tends to equalize the concentrations of the two solutions. According to current electrochemical theory, the solution pressure of the two electrodes is the same, while the osmotic pressure of the zinc ions in the concentrated solution is greater than in the dilute solution. Hence the zinc ions are driven out against the zinc electrode in the concentrated solution, and part with their positive charges. This electrode is therefore positive, and the current in the external circuit flows from the electrode in the denser solution to the other. Such is the universal conclusion among writers on the theory of concentration cells. Thus LeBlanc says: "In such a cell, where the electrode furnished positive ions, the current always flows through the cell from the dilute solution to the concentrated." To the same effect is the following from Prof. Jones' new book on the "Elements of Physical Chemistry." "The electrode in the more concentrated solution is always positive, since metallic ions are giving up their positive charges to it and separating as metal upon it. * * * * In an element of this kind the current always flows on the outside from the electrode which is immersed in the more concentrated solution."

In such a cell there are three contacts of dissimilar substances where electromotive forces may originate, namely, at the two contacts of the liquid and the electrodes, and at the surface of separation between the two electrolytes. When all three sources of electromotive force are taken into account, the formula worked out on the solution-pressure, osmotic-pressure or Nernst theory is the following:

$$E = -0.0002 \frac{i}{n} \cdot \frac{v}{u+v} T \log. \frac{c_1}{c_2}.$$

In this formula i is the van 't Hoff factor of dissociation, u and v the ionic velocities of the positive and negative ions respectively, and c_1 and c_2 the concentrations of the two solutions; n is the valence of the metal ion. Of this equation Lüpke says in his "Grundzüge der Elektrochemie:" "The minus sign in the above formula means that within the concentration cell the current goes from the dilute to the concentrated solution, so that the electrode in the latter is the cathode, and in the former the anode."

Not only is there unanimous agreement relative to the sign of the two electrodes in such a concentration cell, but there does not

appear to be any way by which this formula may be made to give the opposite result. The decisive factor is the osmotic pressures of the positive ions in the two solutions. No appeal to any of the terms in this equation elicits a response showing a current reversal as a possibility. Either the theory is radically wrong, or else the direction of the electromotive force within the cell must always be from the dilute solution to the concentrated.

The novelty in the new concentration cell which I am about to describe lies in the fact that the electrode in the dilute solution is the positive one, and the current flows through the cell from the concentrated to the dilute electrolyte. It is nickel in one of its salts. So far I have tried only the sulphate and the chloride.

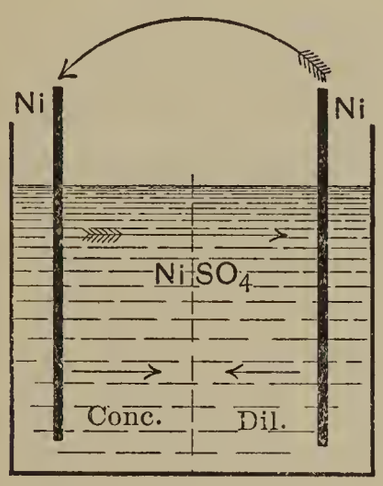


FIG. 1.

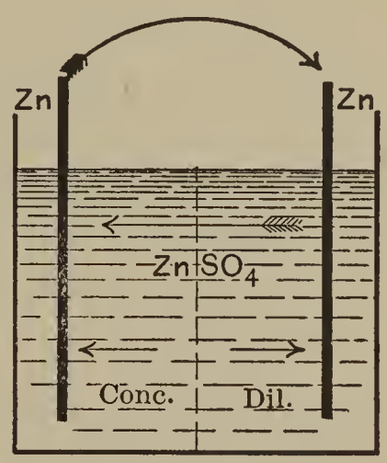


FIG. 2.

Moreover, the electromotive force of this concentration cell is much larger than the accepted formula gives, regardless of its sign. In Fig. 1 the long arrow shows the direction of the electromotive force of the cell and of the current for $Ni—NiSO_4$. The two solutions contained respectively $^1/_{10}$ and $^1/_{100}$ of a gram-molecule to the liter. The short arrows show the direction of the thermo-electromotive force between the metal and its salt solution.

Fig. 2 represents a $Zn—ZnSO_4$ concentration cell. It will be observed that the arrows showing the direction of the electromotive forces are all in the opposite direction to those of the $Ni—NiSO_4$ cell. Chloride solutions give qualitatively the same results. If it be granted that the osmotic pressure theory of a voltaic cell satisfactorily explains the $Zn—ZnSO_4$ concentration cell and others like it, still it entirely fails to give an account of the cell in which nickel electrodes are immersed in solutions of nickel salts.

All of these concentration cells may be accounted for by means of the thermo-electromotive forces existing at the junctions of dissimilar substances. Leaving out of account the thermo-electromotive force at the contact surface of the two electrolytes differing in concentration only, which is usually small, but not entirely negligible, the direction of the current through a concentration cell may be readily accounted for by the two thermo-electromotive forces between the electrodes and the electrolytes. I have found that *the thermo-electric power of a metal and its salt solution increases with the concentration of the solution.* Thus the thermo-electromotive force between zinc and a $^1/_{100}$ normal $ZnSO_4$ solution is 0.00062 volt for 1° C., while for a normal solution of $ZnSO_4$ it is 0.00080. The electromotive force per 1° C., of the $ZnSO_4$ concentration cell is the difference between the two thermo-electromotive forces corresponding to the two concentrations, and is in the direction of the arrow on the concentrated side, or the electrode in the concentrated solution is positive.

For $Ni—NiSO_4$ I have found much higher thermo-electromotive forces. It is about 0.0038 volt per 1° C. for nickel and a $^1/_{10}$ normal solution. For a $^1/_{100}$ normal solution it is about 0.001 volt per 1° C. These are approximate and preliminary values. Since the thermo-electromotive force in the case of nickel and its salts is directed from the metal to the solution, or in the opposite direction to that of zinc, copper, or silver and their salts, it follows that the electromotive force of the nickel concentration cell is directly opposite to that of the other concentration cells heretofore described. Within the cell the current flows from the concentrated solution to the dilute. Moreover, the electromotive force of such a cell is at least ten times as large as that of a $Zn—ZnSO_4$ concentration cell, — altogether too large to come within the Nernst formula.

I have shown in other papers that the temperature coefficient of voltaic cells is completely accounted for by the thermo-electromotive force at the several contacts within the cell. I have now to add that the electromotive force of a concentration cell is rationally explained by these same electromotive forces, or that such a cell is thermal in character. The nickel concentration cell is as readily explained by these indubitable facts as are the older familiar ones. The essential fact in the explanation of concentration cells as a thermo-electric effect, which has not been

observed by any preceding investigator, so far as I am aware, is the increase of the thermo-electric power between a metal and its salt solutions with increase in the concentration. This is the key that unlocks the door to the secret chamber.

DISCUSSION.

MR. C. J. REED. Mr. Chairman, I have been very much interested in this description as it has been given by Dr. Carhart, from the fact that I have corroborated his results already without knowing it. I have obtained results with a nickel concentration cell which agrees with what he says; and being unable to explain those results I concluded they were due to my faulty experimenting. While experimenting with cells of this type, which I have brought here for exhibition, I obtained metallic deposits of Ag, Pb, Cd, Zn, Cu, and many other metals, in all cases the metal being deposited from the strong solution as required by the rule. But with Ni I could get no deposit in the stronger solution and there were indications of a current in the opposite direction. I could not account for this and concluded it was due to impurities. But these investigations of Dr. Carhart explain my results.

DR. E. F. ROEBER: Mr. Chairman, this is very remarkable from one point of view. When you look at other concentration cells you will find the current is always in such a direction that the concentrations tend to become equal; that the dilute solution becomes more concentrated and the concentrated solution more dilute. It is different in Professor Carhart's cell. Nickel is taken out at the dilute side, and is dissolved from the anode on the concentrated side; hence the dilute side would become still more dilute and the concentrated side become more concentrated.

MR. C. HERING: It almost seems as if this would lead to perpetual motion.

DR. CARHART: There is no doubt about the fact.

MR. REED: How would it lead to perpetual motion?

MR. HERING: Instead of the action tending to equalizing the concentrations, the current seems to make the dilute solution more dilute and the concentrated one more concentrated. A puncture through the diaphragm would allow the solutions to mix mechanically, and

the action would then keep up indefinitely, thus making a sort of perpetual motion. As that is probably impossible, it follows that there are probably some limiting conditions which we do not know about, at which the action will cease.

Mr. Reed: The energy must come from heat. It proves there is thermoelectric action.

Mr. Hering: Then such a cell would abstract heat from the air and consume no materials. It would produce electric energy out of the heat from the air. There is another cell that is supposed to do this; it consists of amalgamated zinc and unamalgamated zinc in zinc sulphate.

Dr. W. D. Bancroft: The experiments do not agree with the Nernst formula; but that formula applies only when the heat effect is zero. If the heat of dilution were sufficiently large and had the proper sign, the effect due to this might more than counterbalance the effect due to the concentrations. In the sodium amalgam cells the two effects have the same sign and the electromotive force is double the calculated value. This is a possible explanation of these unexpected results. It is also possible that there is a time element and that a secondary reaction takes place, analogous perhaps to the hydrolysis of stannic chloride.

President Richards: Although this is extremely interesting, the Chair will have to limit the discussion. I will ask Professor Carhart to close the discussion.

Dr. H. S. Carhart: The Society will remember I am not here to verify the ionic theory at all, but simply to show that the accepted explanation of these cells is not correct.

As to the other point, about the heat of dilution, I want to hold to this: that whatever may be the facts in that respect in this new cell, the direction of the electromotive force is opposite to that of cells to which the Nernst theory applies. Now, whether this is accounted for by the heat of dilution or not, I am unable to say, but I think not.

Discussion communicated after adjournment.

Dr. E. F. Roeber: I will first give an exact proof of the statement made by me in the discussion that if this interesting cell of Professor Carhart is really what it is called, namely, a concentration cell, then the concentrated solution must become more concentrated and the dilute solution more dilute during discharge. If

this cell is really a concentration cell, the same amount of nickel goes into the solution from the anode, as is deposited upon the cathode, and the only resulting change is a change of the concentrations of the two solutions. Should the chemical action at the electrodes be something different, then the resulting change in the cell would not be merely a change of the concentrations, and the cell would not be a true concentration cell.

Let n be the transport number of the anion, then if the current flows in the cell from the concentrated to the dilute solution, the following changes take place during the passage of $2 \times 96{,}540$ coulombs: one (bivalent) gram-molecule Ni passes from the anode into the concentrated solution, one gram-molecule Ni is deposited from the dilute solution upon the cathode, and through any cross-section of the electrolyte, n gram-ions SO_4 pass in the direction from the dilute to the concentrated solution and $1-n$ gram-ions Ni in the opposite direction. The resulting change is therefore that in the dilute solution n gram-molecules $NiSO_4$ disappear and in the concentrated solution n gram-molecules are formed. Hence, as n is necessarily positive, the dilute solution becomes more dilute and the concentrated solution becomes more concentrated.

Now, I fully concur in the opinion expressed by Mr. Hering, that this would lead to very serious thermodynamical consequences. Indeed it can be easily shown that we thus come into conflict with the second principle of thermodynamics. For instance, imagine the following cycle: connect Professor Carhart's cell to a small electric motor and let the cell discharge; it would drive the motor and perform mechanical work; in the cell the dilute solution would become more dilute and the concentrated solution more concentrated. Now break the circuit, and let diffusion act; it would act in such a way that it tends to equalize the concentrations; it would therefore bring the system back to its initial condition. We may assume that while this cycle is performed, the cell is contained in a large reservoir of heat, of the same temperature as the cell at the start of the cycle. When the cell (or a part of it) tends to become cool, heat will pass from the reservoir to the cell. When the cell (or a part of it) tends to heat, then heat will pass over to the reservoir. The reservoir is assumed to be so large that the change of its temperature, due to the transportation of heat to or from it,

is infinitely small. In this way the temperature of the cell and of the reservoir is kept constant throughout the cycle, and the whole cycle is essentially isothermic. What do we accomplish by means of this cycle? Mechanical work is performed by the motor. Therefore an equivalent amount of another form of energy must disappear during the cycle. The cell itself is in exactly the same condition at the end of the cycle as at the start; hence its internal energy is also the same at the end as at the start. It is thus evident that the heat reservoir must contain less heat at the end of the cycle than at the beginning; the heat which has disappeared in the reservoir has been changed into mechanical work. Thus, our system represents a machine which while undergoing cyclic isothermic changes (that is, changes at constant temperature) transforms heat directly into mechanical work, without any other quantity of heat passing at the same time from a reservoir of higher temperature to a reservoir of lower temperature. Such a machine, however, is impossible according to the second principle of thermodynamics.

It follows that the second principle of thermodynamics requires that in any concentration cell the current in the cell during discharge must flow in the direction from the dilute solution to the concentrated solution. Hence, Professor Carhart's cell—if it is a concentration cell—strikes directly at one main root of modern natural science: at the second principle of thermodynamics. It is in contradiction with Professor Nernst's theory of concentration cells, only because the latter is based upon the second principle of thermodynamics; that this is indeed the cornerstone of Nernst's theory, could be easily shown by an analysis of his theory and is very evident from the way in which Professor Planck has arrived at the same formulas as Nernst.

If therefore the cell of Professor Carhart is a true concentration cell, it becomes an extremely serious matter. But before far-reaching conclusions should be drawn from it, it should be clearly borne in mind that Professor Carhart has so far established only one fact: that the direction of the electromotive force of his cell is so that the current in the cell flows from the concentrated to the dilute solution. Professor Carhart states himself that he has not yet ascertained whether the concentration changes are such as they must be under the assumption that he has indeed a concentration

cell. Therefore, it is quite possible that the chemical changes at the electrodes are not what they are assumed to be: the combination of anodic nickel with SO_4 ions, and the deposition of the same amount of nickel upon the cathode. If what takes place at the electrodes of Professor Carhart's cell is something different, then my conclusion regarding the concentration changes does not apply; there is no longer a contradiction with the second principle of thermodynamics nor with Nernst's theory; in this case the cell would not be a true concentration cell. In my opinion this will be found to be the correct explanation of the apparent contradiction.

PROFESSOR CARHART: A concentration cell of the first type is always described as composed of two electrodes of the same metal, dipping into two differently concentrated solutions of a salt of this metal. This is the definition of Nernst himself ("Theoretische Chemie," p. 666). This description exactly describes my nickel—nickel sulphate or nickel—nickel chloride cell. If Dr. Roeber wishes to change the definition of a concentration cell to make it correspond with Nernst's equation for the electromotive force of such a cell, then the literature of the subject will have to be revised, if his suggestion is accepted. The fact is that the energy of the current derived from a concentration cell, as all the formulas show, is chiefly at least thermal in origin. In explaining the direction of the electromotive force of such cells as the resultant of all the thermoelectromotive forces in the cell, I find no such difficulty as the Nernst theory encounters in the new cell which I have described. I may now add a fact that was not known to me at the time my paper was read, that the same explanation of the direction of the electromotive force applies to concentration cells in which the electrodes are two amalgams of two concentrations, the solution being the same throughout. I shall have further contributions to make to this interesting subject at the next meeting of the Society.

A paper read at the Inaugural Meeting of the American Electrochemical Society, Philadelphia, April 4, 1902, President Richards in the Chair.

THE MANUFACTURE OF BISULPHIDE OF CARBON IN THE ELECTRIC FURNACE.

By Edward R. Taylor, Penn Yan, N. Y.

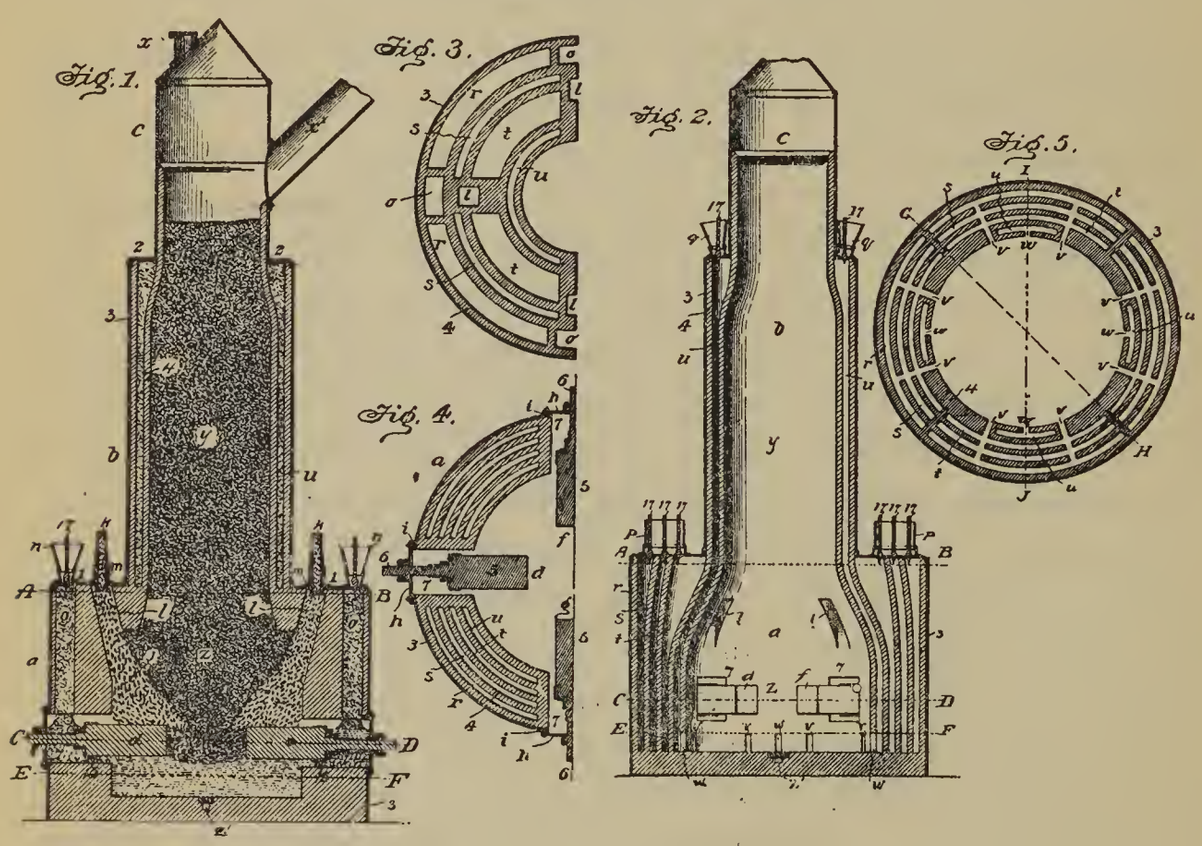
Having been engaged in the manufacture of the bisulphide of carbon for about twenty-five years, and quite familiar with the disagreeableness of former methods, more than twenty years ago the author turned his thought to a possible electric method as the most feasible means of placing the production upon a better basis. Because of these disagreeable features, at least, six different parties in the country have in that time given up its manufacture in disgust, and the author should have done so himself, but was unable to let go and, therefore, set upon himself the development of a better process, which has been the careful study of years.

In any process of heat derived from combustion, the carbon and sulphur, which are the reacting materials, must be separated from the combustion chamber, or the very material required would be oxidized to other products. This separation was effected in retorts of fire-clay or iron, heated externally, with suitable provision for the removal and condensation of the product. Clay retorts are more enduring than iron, but have to be thicker, and, being poorer conductors of heat, have their disadvantages to offset their longer endurance. With either of them a very small fraction only of the heat developed by combustion becomes effective in combining the carbon and sulphur which, as is well known, is a process requiring the addition of heat to effect.

Moreover, these retorts must be limited in size to be effective at all in the accomplishment of the work, and the building in which they are placed becomes like an oven with an atmosphere anything but agreeable to be in.

To overcome these many disagreeable features, as well as to apply the heat inside where it is required to do the work, I gave early thought to the development of an electrical process. This has proved in practice to be as practical, cleanly and desirable as my fondest hopes ever pictured.

The first furnace for this purpose was surrounded with an external shell of iron in which the sulphur was melted by heat radiated from the inner metal shell of the furnace, and admitted to the furnace proper in the melted state by means of valves. This practice was found to be inconvenient and unsatisfactory, and arrangements were made to substitute brick walls for those of metal, and to feed the sulphur directly to the furnace in the cold state, surrounding the interior so completely as practically to



make a blanket of sulphur which in melting carries the heat absorbed back into the furnace. So effective is this regeneration that the larger the production of goods the cooler is the outside of the furnace, and the more effective the utilization of the heat generated in the interior in the production of bisulphide.

In the building containing the furnace, there are no unpleasant gases or other features that are in the least disagreeable, and the whole building is at all times comfortable to be in in every respect. If necessary other operations could be conducted therein with entire satisfaction.

The life of the electrodes received my early consideration, and arrangements were made to keep them constantly and automatically supplied with broken carbons, which provide the electrodes with a large contact surface, against which they lie and from

which the broken carbons taper off to the interior of the furnace, where the greater resistance converts the electrical energy into heat just where it is required for effective work. All of this is made clear by the drawings.

The sulphur rises in the bottom of the furnace and its height is regulated by feeding cold sulphur into the surrounding chambers according to requirements, and being a non-conductor of electricity becomes an important factor in regulating the current passing through the furnace.

The induction type Stanley generators, of 330 kilowatt capacity each, furnish the electricity without the intervention of transformers, the current being easily regulated by the field and exciter rheostats.

With regular supplies of electricity and materials required in the furnace nothing can exceed the ease and satisfaction of its operation, which is continuous for many months together.

DISCUSSION.

Dr. H. S. Carhart: I wish to inquire about the wasting away of those carbon electrodes.

Mr. Taylor: The waste of the electrodes is very small. The area of the carbon you see indicated in the lower left-hand corner is twenty inches. They are 48 inches long and each represents a surface of 20 square inches; they are very large and their conductivity is ample.

President Richards: I think it is well known that this furnace of Mr. Taylor's has practically revolutionized the manufacture of carbon bisulphide in this country, and the size of the furnace is a revelation of what may be expected in the size of electric furnaces in the future.

A paper read at the Inaugural Meeting of the American Electrochemical Society, Philadelphia, April 4, 1902, President Richards in the Chair.

CURRENT ELECTROCHEMICAL THEORIES.

By Louis Kahlenberg.

The present stage of the development of electrochemistry makes the first general meeting of the American Electrochemical Society an opportune time to take a brief survey of existing electrochemical theories. It is not the purpose of this paper to set forth a new theory, but rather to take an inventory, as it were, of existing hypotheses, in the hope that thereby experimental research may be stimulated and guided into such channels as seem to promise the best returns for expended effort.

It is quite safe to state that the Grotthuss theory, which, of the various early attempts, was the first to give a plausible explanation of the phenomena observed during electrolysis, is no longer held. This hypothesis was fairly generally accepted until about the middle of the nineteenth century, when electrolysis was studied in the light of the, then recently discovered, laws of conservation and transformation of energy.

It was in 1857 that Clausius pointed out the difficulties that the Grotthuss theory meets when viewed from the standpoint of the second law of thermodynamics. He consequently proposed a new theory which involved an application of the kinetic hypothesis to electrolytes. Like Williamson, in his explanation of the process of the formation of ether from alcohol and sulphuric acid, Clausius assumed the molecules of liquids in constant motion caused by heat. He considered that in the bombardment of the molecules of an electrolyte, interchanges of the constituents of the different molecules take place; in other words, that decompositions and recompositions continually occur which at any instant, however, affect only a small percentage of the total number of molecules present. He then conceived that the electric current simply gave these decompositions and recompositions a general direction or trend, and at the same time facilitated them. He was thus able to explain why even a slight electromotive force suffices to send a current through an electrolyte, and at the same

time, he did away with the very artificial idea of the regular orientation and arrangement that the molecules undergo during electrolysis as conceived by Grotthuss. It is doubtless true that the theory of Clausius is still regarded with favor by a goodly proportion of the more conservative class of scientists, though they adhere to the theory at the risk of being called old-fashioned.

The theory of Arrhenius, or the so-called theory of electrolytic dissociation, is the latest electrochemical hypothesis. It has existed for a decade and a half, and though far from universally accepted, it has many enthusiastic adherents. Unlike the earlier electrochemical theories, the hypothesis of Arrhenius is not founded solely, or even mainly, on the phenomena of electrolysis. While the theory of electrolytic dissociation offers an explanation of the passage of the current and the changes that occur at the electrodes, it really sprang into being from a study of the electrical conductivity of aqueous solutions of acids, salts and bases on the one hand, and the vapor-tensions, freezing-points, boiling-points or so-called osmotic pressures of such solutions on the other hand. In 1887 van't Hoff emphasized the analogy that exists between gases and dilute solutions, by showing that in some cases the relation that exists between temperature, volume (*i. e.*, concentration) and osmotic pressure of solutions may be approximately expressed by means of the gas equation. In other cases, however, he found that this could not be done, the osmotic pressure being too great. Arrhenius then pointed out that the latter cases were solutions that conduct electricity; and calling attention to the fact that their so-called molecular conductivity increases with the dilution, he sought to explain the abnormal osmotic pressure and at the same time the increase of the molecular conductivity with the dilution, by assuming the dissolved molecules to be dissociated to a certain, generally very considerable, extent into part-molecules. He conceived the latter to be statically charged with electricity, the basic radicals with positive and the acid radicals with an equivalent amount of negative electricity. The sweeping generalization was then soon made that in every case when the osmotic pressure of a solution exceeds that required by the gas law, the solution is an electrolyte, and *vice versa*. As a matter of fact, however, experimental research has developed that there are numerous cases in which the osmotic pressure does not exceed that required by the gas law or

is even much less than is required by the gas equation, and yet such solutions are often good electrolytes. And again, it has recently been shown in this laboratory[1] that when the osmotic pressure, as indicated by boiling-point determinations, is abnormally high, the solution is by no means necessarily an electrolyte. Furthermore, the molecular conductivity of some electrolytes diminishes as the dilution increases. The writer has no intention of detailing here all the special cases that cannot be harmonized with the theory of electrolytic dissociation. The work along this line has been presented in a series of articles in the *Journal of Physical Chemistry* to which the reader must be referred. Suffice it to state that if the facts that are at hand at present had been known in 1887, it seems quite safe to say that the theory of electrolytic dissociation would not have been born. The excellent researches of Walden[2] on the behavior of solutions in liquid sulphur dioxide, and particularly the very recent work of A. Smits[3] on the vapor-tensions of dilute solutions of electrolytes will demonstrate to any unbiased reader that the theory of Arrhenius is untenable. To be sure, these investigators and also some others still try to "harmonize" their results with the theory of electrolytic dissociation, but their efforts at this remind one strongly of the attempts of the ardent advocates of the old phlogistic theory, when they sought to harmonize the fact that bodies are heavier after they are burned, with the hypothesis they wished to uphold at all hazards.

The theory of Arrhenius has done much toward stimulating research in electrochemistry, chemistry in general, and even in physiology. Due credit must be given it on this account. But the facts that flatly contradict the hypothesis are now so numerous that its doom is sealed. With regard to the so-called modern theory of solutions (which is so inseparably connected with the theory of Arrhenius, and which is based on the analogy between gases and dilute solutions) it must be said that it too has done very much toward inciting experimental inquiry. But it is also clearly evident, that by assuming association or dissociation, or both simultaneously, in the case of the solute of a dilute solution for no other reason than to make the behavior of the solution conform to the Avogadro-van't Hoff hypothesis, is systematizing

[1] J. Phys. Chem., **6**, 45 (1902).
[2] Bull. Acad. Sci. St. Petersburg **15**, 17 (1901).
[3] Ztschr. phys. Chem., **39**, 385 (1902).

matters at too great an expense. It is in fact nothing more than to arbitrarily make the behavior of all solutions conform to a Procrustean bed. Again, since the gas equation theoretically applies only to exceedingly dilute solutions, the theory of solutions has unquestionably retarded the work on concentrated solutions very greatly; and in so far it has been a bar to true progress toward a real understanding of the very important subject of solutions. Similarly the theory of Arrhenius has directed particular attention to the electrolytic phenomena in dilute solutions. I think the *facts* at present known are sufficient to warrant the expression of the opinion that for a true conception of the nature of solutions and of the process of electrolytic conduction it is unfortunate that the efforts should have been thus almost exclusively directed toward dilute solutions. These represent simply a limiting case, and very likely the most complicated case. But it is not intended to enter upon a consideration of the subject of solutions here; it has only been mentioned because of its intimate connection with the theory of electrolytic dissociation.

Can any one doubt that Faraday was correct in his contention, that a system like that of two silver electrodes dipping into molten silver chloride represents the simplest electrolytic cell? Here, as the current flows, silver is deposited on one plate and dissolved from the other; and only two chemical elements are concerned in the process, and these in the form of one element and one simple compound. The electrolyte and the plates remaining the same in character as the current passes, no changes in concentration around the electrodes occurring, there is no counter electromotive force set up in the cell. Until such a simple case as this is thoroughly understood, does it seem rational to study with great care the changes in concentration that occur in electrolytes around the electrodes in dilute solutions, with the intention of drawing from the results so secured conclusions as to the relative speed of the ions? After considering such a simple case as that just mentioned, does it not seem far more probable that such differences in concentration around the electrodes in the case of solutions occur because of the presence of the solvent, and that they are really only secondary in character, resulting from the chemical changes that go on at the electrodes and from the diffusion processes that these changes cause?

Unfortunately for the cause of electrochemistry, attention has,

of recent years, been directed only to a slight extent to the processes of electrolysis in molten salts. The theory of electrolytic dissociation, to be sure, has boldly assumed the presence of free charged ions in molten salts, but there are clearly no experimental facts to warrant this assumption. The latter has simply been made because free charged ions have been supposed to be present in conducting *solutions*, and so they "must also cause" the conduction of molten salts. What difficulties are met in trying to explain the electrolytic behavior of molten salts from the standpoint of the theory of electrolytic dissociation and its consequences, is well illustrated in a number of excellent experimental articles that have of recent years appeared in the *Zeitschrift für anorganische Chemie*.

Although Faraday's law forms the basis of electrochemical work, his views as to the nature of electrochemical action have remained almost entirely confined to the volumes of his experimental researches. Recently, C. J. Reed, in an article published in the *Journal of the Franklin Institute* (May–June, 1901), revived some of Faraday's ideas; however, in his description, he went into such details that the scheme of the orientation and arrangement of the molecules remind one strongly of Grotthuss' theory, and it is likely that Faraday, in his characteristic manner, would have pronounced it as rather too significant. Faraday has truly said that experimental work is a great disturber of preconceived theories. He was no worshiper of hypotheses, he used them simply as a means for gaining new truths and never showed the least reluctance to abandon a theory whenever it seemed to him that the facts required it. It is to this attitude of mind that his brilliant success as an experimental investigator was due in a large measure. No doubt the fact that Faraday was never so engrossed with any one theory that he became an ardent advocate or expounder of it, explains why his theoretical views did not finally find a place in text-books.

With regard to the energy changes that occur during electrolytic processes, there is little or no difference of opinion. It is well recognized that any explanation of electrochemical action must take cognizance of the laws of thermodynamics. In this connection the monumental work of Helmholtz on the electromotive force of the galvanic cell looms up in all its splendor, and the theory of Nernst appears after all but little more than an artificial

reproduction of the ideas of the former. The real difficulty lies in producing an adequate mechanical picture of the electrochemical process—a mechanical conception which shall adequately represent the relations between electricity and the gross matter undergoing change. In seeking such a mechanical conception, it is always well to bear in mind that our atomic and molecular notions are themselves after all only hypotheses, invaluable though they have been and still are. Our knowledge of electricity has been greatly extended of recent years by splendid researches, and yet we have no adequate mechanical conception to account for electrical phenomena that are unaccompanied by chemical changes. Indeed it is being counseled at present that it is unwise to waste time in seeking suitable mechanical explanations for physical phenomena, that it suffices to rest content when the energy changes in the processes are properly accounted for in conformity with the laws of conservation and transformation of energy. These counselors do not always live up to their own suggestions. And while their advice may perhaps serve as some consolation, seeing that we clearly do not at present have an entirely adequate mechanical conception of electrochemical processes, or even of the simple process of electrical conduction in a wire, yet it must be borne in mind that the advancements in physics and chemistry have, after all, largely been made by the aid of mechanical theories. Furthermore, it is quite possible that a far more adequate mechanical explanation of electrochemical processes than we have may yet be originated, which, acting as a new working hypothesis, may lead to the discovery of many new facts useful to mankind. No doubt the enthusiastic membership of the American Electrochemical Society will contribute its fair share toward the progress of this work.

Laboratory of Physical Chemistry,
University of Wisconsin,
Madison, March, 1902.

DISCUSSION.

Professor Richards: Although Professor Kahlenberg is not here, yet the discussion of his paper is in order and will be replied to, probably, by Professor Kahlenberg in the transactions of the Society or by mail.

Dr. H. S. Carhart: Mr. Chairman, I wish to call attention to one point only that appears in this paper, and that is the reference to the Helmholtz equation. I wish to call attention to an American who has done scientific work, but not in his own country, in connection with this matter. While there is no man who has higher respect for the memory of Helmholtz than myself, having had the privilege of working with him for a time, yet we ought to emphasize the fact that the relation expressed by the Helmholtz equation was first published by Professor Gibbs, of New Haven.

Dr. W. D. Bancroft: I am sorry to contradict you. I know that that statement appears in many text-books, but you will find that Gibbs simply showed that we had to take into account the change of the entropy, and showed where the explicit assumption had been made in Thomson's law. The equation as it stands is Helmholtz's; the qualitative generalization is due to Gibbs.

A paper read at the Inaugural Meeting of the American Electrochemical Society, Philadelphia, April 4, 1902, President Richards in the Chair.

A ZINC-BROMIDE STORAGE BATTERY.

By Herbert H. Dow.

A very good storage battery may be made with zinc and carbon electrodes, and a zinc-bromide electrolyte. In charging, zinc is deposited on the zinc electrode, and free bromine is liberated at the carbon electrode. In discharging, the bromine disappears and the deposited zinc is dissolved. Probably only one reaction takes place, namely, $Zn + Br_2 = ZnBr_2$. This is an extremely simple operation as compared with the complicated reactions that take place in the ordinary lead cell, and the fact that the voltage is the same when slightly charged and when heavily charged, would indicate that the reactions under these extreme conditions are identical, whereas, in the lead battery the voltage is very materially different when the cell is nearly charged from what it is when but partially charged.

The voltage is a trifle above 1.7, and is the same on discharge as it is on charge, and does not appear to change with variations in the strength of the electrolyte. We have not done enough work on the cell to know whether this constancy of voltage will make it adapted for a standard cell. Professor D. C. Miller, of the Case School of Applied Science, is now investigating this subject. If it proves to give a constant voltage under conditions that are easily obtained, it will have many advantages over any standard cell yet brought out. It can be constructed anywhere on very short notice, as it is no more complicated than the simplest form of primary battery.

DISCUSSION.

Mr. C. Hering: Have you used a porous partition?

Mr. H. H. Dow: No porous partition is necessary.

Dr. H. S. Carhart: What keeps the bromine?

Mr. Dow: If the cell is used periodically it acts just like the Daniel's gravity cell, the bromine nearest the zinc is used up first, not that next the carbon. If it was charged for ten minutes and used for one minute, and then charged again for ten minutes and used for one or more minutes, and so on, indefinitely, the bromine would always be plated out next the carbon and used from that part of the bromine solution next the zinc. In other words, the bromine that had diffused the farthest would be used first, and the discharges would be at short enough intervals to prevent any bromine diffusing far enough to come in contact with the zinc electrode.

Mr. C. J. Reed: I believe a cell of that kind was described about ten or twelve years ago, I think it was by Professor Crocker, but am not certain. I remember distinctly a patent describing a cell with zinc, bromine and carbon, about ten or twelve years ago. I am very certain that was the exact construction, and that the carbon was at the bottom and the bromine was formed in the lower part.

Mr. H. Rodman: There is such a patent, I am sure.

A Member: What is the weight per horse-power of such a cell?

Mr. Dow: I might say, in an ordinary cell that has its energy stored in the form of oxygen, the weight is only eight as compared with eighty when the oxidizing force is bromine. That is, there is ten times the capacity in the cell in which the oxidizing force is stored in the form of oxygen to what there is when the oxidizing force is stored in the form of bromine. It, therefore, appears on the face of it, as though the weight of the cell must be very great, but when the bromine exists as free bromine, and when the oxygen exists as an oxide of lead, the weight of the lead has also to be taken into consideration; so that under those circumstances the discrepancy is not so great in the theoretical possibilities of two cells.

The great commercial disadvantage that we have found in it is, that the zinc will deposit in crystals, and the crystals will cross the cell and short-circuit it, unless it is periodically charged and discharged; in that case the crystals will dissolve more readily than the plate back of it. There may be commercial applications of it where it is used in work where there is a charge and discharge at frequent short intervals.

In the commercial form of cell there is one carbon plate about a foot square and a sixteenth of an inch thick. On that is placed a piece of asbestos saturated with zinc bromide solution, and on the top of that a zinc plate, and then a carbon plate, and a pile built up in that manner.

Mr. E. A. Sperry: What is the ampere capacity of such a cell of that size?

Mr. Dow: I don't know, but it seems to be limited only by the temperature.

Mr. Sperry: What is the temperature in one of that size?

Mr. Dow: In one about three inches square that I tried on a fifteen ampere instrument, the needle went over and hit the peg; and I put my finger on it and burnt my finger with the wire. Of course, there was a short path and it discharged almost instantly.

Mr. Hering: Is there not considerable leakage around the carbon plates?

Mr. Dow: I might say I think there is leakage in the cell itself, although the plates are all paraffined. It is due to the fact that it is impossible to make the plate entirely free from pores by boiling in paraffine. The volume of the liquid paraffine is much greater than the volume of solid paraffine; it therefore follows that a carbon plate filled with liquid paraffine will be somewhat porous when the liquid solidifies so that there will be a very measurable amount of loss due to the current passing through the whole series of pores in the different wet plates. I don't know what that amount of loss is, but it is reasonable to suppose that it is an item worth considering.

A paper read at the Inaugural Meeting of the American Electrochemical Society, Philadelphia, April 5, 1902, President Richards in the Chair.

CONTINUOUS ELECTROLYSIS OF SOLUTIONS OF METALS.

By N. S. Keith.

The title refers to the treatment by electrolysis of solutions of metals obtained in various ways, for the purpose of continuously separating one, or more, of the constituent metals, and at the same time leaving the thus depleted solution with a constitution that makes it a suitable solvent of more of the metal from a source of supply, to be again electrolyzed in a continuous cycle of operation. It also refers to obtaining metals from their solutions in waters flowing from mines.

These latter may be termed *natural* solutions, and the former *artificial* solutions. I have selected solutions of copper for consideration in this paper, because they are the most important in the way of quantity.

In the art of metallurgy, the chief natural solution is that of cupric sulphate, flowing from mines which yield sulphides of copper and iron, such as chalcopyrite, cubanite, bornite, etc., more or less mixed with pyrite and pyrrhotite. These mixtures of minerals, with access of heat, oxygen, and water suffer decomposition with formation of $H_2SO_4 + CuSO_4 + FeSO_4 + Fe_2(SO_4)_3$, etc., which are dissolved in the water from the mine, flowing or being pumped therefrom, often to absolute waste; but frequently these waters have been caused to pass in contact with scrap iron for the recovery by precipitation, called cementation, of a very considerable part of their contents of copper. Theoretically, 56 pounds of iron should precipitate 63.5 pounds of copper from a solution of $CuSO_4$, but when the solution contains free acid and some ferric sulphate, the amount of iron used is much larger, being, in practice, about twice that quantity. Take, for example, these equations:

$$CuSO_4 + Fe_2(SO_4)_3 + 2Fe = Cu + 4FeSO_4$$

or

$$CuSO_4 + H_2SO_4 + 2Fe = Cu + 2FeSO_4 + H_2.$$

These equations are simple. The fact is, however, the re-

actions are much more complicated, as they must be with the access of oxygen of the air, and the presence of carbon in the iron, as is in evidence when the clean-up comes. Instead of a pure copper deposit, as would be the case with a pure copper solution and pure iron, we find but from 50 to 70 per cent. to be copper, and that in a powder, and the remainder to be oxides of iron, sand, graphite, and other matter out of place, tersely called "dirt." This mixture is called "cement copper," and goes to the smelter.

This copper costs, independent of superintendence, interest, and the like, the price of the scrap iron, the labor of placing the iron, cleaning-up the deposit, and the smelting. Scrap iron is worth $15 per ton in Philadelphia or New York, and may be $50 at the mine. At, say, one cent per pound for iron, copper by cementation costs about two and three-quarters cents per pound in the pig, when produced from mine waters costing nothing.

By electro-deposition the same quantity of copper can be produced as marketable cathode copper at less than three-quarters of a cent per pound, where power for the generation of electricity costs $60.00 per horse-power year of 360 24-hour days; or for less with water-power. But with this latter treatment it is desirable that the copper be extracted by a continuous operation from the liquid as it flows from the mine.

Next in greater importance is the electrolysis of the artificial solutions, obtained by lixiviating ores having three per cent., or less, of copper, and which are prepared for such lixiviation by methods of oxidation, such as (1) long-continued (often for years) submission to the action of heat, air and water in immense piles; or (2) by the action of heat and oxygen in furnaces.

In the former case the lixiviation takes place coincidently with the oxidation, and the lixiviate flows from the pile of ore onto iron scrap placed in long troughs and boxes, as in the case of the treatment of natural solutions. The ores consist of sulphides of copper and iron, in the main, in silicious gangues, frequently carrying some calcium carbonate such as calcite. The chemical reactions are illustrated by the following equations:

$$Cu_2S + 2Fe_2S_3 + CaCO_3 + O_{35} = 2CuSO_4 + 4FeSO_4 + CaSO_4 + 2H_2SO_4 + CO_2,$$

or

$$Cu_2S + 4FeS_2 + CaCO_3 + 2H_2O + O_{33} = 2CuSO_4 + 4FeSO_4 + CaSO_4 + 2H_2SO_4 + CO_2.$$

In by far the larger number of cases the iron sulphides far exceed in quantity the copper sulphide and the alkaline earthy constituents, so that the reactions which take place to form H_2SO_4 furnish enough of the acid to unite with all of the earthy alkaline materials, as well as to furnish acid for the copper, which its own combined sulphur would insufficiently supply.

Then substantially, the lixiviate, after the above treatment, consists of an acid solution of cupric and ferrous sulphates. This is likewise treated with iron to obtain the contents of copper.

In the second case of preparation of the ore for obtaining an artificial solution of copper the cupriferous materials, constituted as in the first case, are powdered and roasted in various of the mechanically operated roasting furnaces, well known in the art, with a result consisting of a powder containing besides the gangue varying quantities of cupric sulphate, cupric oxide, perhaps some cuprous sulphide from imperfect work, ferrous and ferric oxides and sulphates, and maybe some calcic sulphate.

When roasting for lixiviation ore which contains copper mainly as carbonates and oxides, with some chalcocite (cuprous sulphide) and no, or an insufficient quantity of, other sulphides, there not being enough of the sulphur constituent to unite with oxygen to sulphate the copper, it is necessary to mix with the ore either sulphur, other sulphides, or sulphates, if it be desirable to sulphate the copper contents to make it soluble in water. Chalcocite (Cu_2S) will not be changed to sulphate ($CuSO_4$) by roasting alone, because there is not sulphur enough to supply the equivalent for the formation of cupric sulphate. And, furthermore, when heated to a temperature much below red it is decomposed directly into metallic copper and free sulphur.

These roasted ores are generally lixiviated with a solution of sulphuric acid, and, until recently, the copper from the lixiviate has been obtained by iron precipitation. But in these cases the copper precipitate costs as much as in the case of the like precipitation from natural solutions, and in addition the price of the acid used for dissolving the copper, as well as some iron, which is always a constituent of the ore. This loss is equal to quite three pounds of commercial oil of vitriol per pound of copper obtained. This acid is worth from $9.00 to $20.00 per ton, or more according to locality of the works. Take it at $10.00 per ton, there is added to $2^3/_4$ cents per pound (the estimated cost of cop-

per by iron from natural solutions) $1\frac{1}{2}$ cents per pound for acid, thus making the total cost of copper obtained by lixiviating roasted ores about $4\frac{1}{4}$ cents per pound for iron, acid, melting and labor.

In view of the preceding facts it is evident that a method which avoids the wastes, and is otherwise less expensive, adds just that much to the profits of the miner; or, maybe, supplies a profit in place of a loss. The electrolytic is that kind of a method.

In the electrolysis of a solution for the purpose of obtaining one of its metal constituents in reguline condition, to practical exhaustion, the main requirement is that the density of current be regulated to the amount of that metal present in the electrolyte, and to the presentation of ions of that metal to the cathode. As the amount of metal in the electrolyte must be a continuously decreasing quantity, it is evident that the density of current must be correspondingly decreased during the process of depletion. Heretofore this has been accomplished by carrying on the electrolysis on a fixed quantity of electrolyte by decreasing the current with the decrease in the metal strength of the electrolyte until nearly all, so far as practicable, of the metal had been deposited.

This plan, it is obvious, is expensive and difficult especially owing to the necessity of decreasing the output of current from the generator by changes of speed and the use of rheostats and other devices, all costly in time, labor, attendance, power absorption, etc. Then again, the plant is not worked, on the average, to but one-half of its capacity at the maximum rate. Starting say, with a density of current equal to 20 amperes per square foot of cathode surface, that density is retrogressively decreased to 1 or 2 amperes, in order to insure the deposition of reguline metal at the last stages of the process. Then the depleted electrolyte is drawn from the vats, and they are again filled with strong solution for the same course of procedure.

The writer has devised and operated an arrangement of electrolytic vats, whereby the above serious difficulty is entirely obviated, and which allows of the continuous electrolysis of solutions of metals for obtaining the metals in a reguline state. The strong solution is caused to flow into the first of a series of any desired number of electrolytic vats, and from that first through all of the others successively, and out of the last of the series in its fully depleted condition.

The vats have in each the suitable number of electrodes connected up in multiple as a set, and the several, or many, sets of electrodes are connected in series. In the first vat are enough electrodes to have a cathode surface proportioned to the supply, and to the permissible density of current necessitated by the strength in metal of the solution flowing into it. In this vat is the minimum number of electrodes, and in the successive vats of the series there is a progressive increase of electrodes, till the last where there is the maximum number of electrodes, where the minimum density of current is requisite. In the last, as well as in the first, and all others, the cathode surface is proportioned inversely to the strength in metal of the electrolyte.

Of course there is a practical limit to this increase of electrodes. Fortunately, in continuous work of dissolving a metal from materials in a separate place from that in which it is electrolytically deposited, it is not necessary to completely deplete the solutions of its metal, because the depleted solution is used again as a solvent of more metal from the ore, except in the case of natural solutions. In this case it is desirable to obtain as much of the metal as possible without the last parts costing more than they are worth.

The anodes must be insoluble, and as nearly indestructible as possible. With sulphate solutions they may be of lead. If a constant electric stress be kept between the anodes and cathodes, equal to the counter-stress which tends to sulphate the anode when the vats are at rest, that is, when no current is passing, no sulphating will occur. But the probable periods of rest in a well-established plant are each of very short duration—practically *nil.*

Anodes of carbon, graphite, and graphitic carbon suffer oxidation and disintegration—the graphitic much less than do those known as battery carbons. Whether there is any true solvent action on the carbon is problematical. The electrolyte becomes very dark-colored, not alone from suspended carbon, for the filtered electrolyte is very dark in color, and carbon is deposited therefrom on the cathode. This carbon deposit does not alloy with the copper deposit, but seems to remain as a powder upon the cathode surfaces, while copper is deposited under it.

The cathodes may be primarily of lead. But as soon as any copper is deposited on the lead they become, so far as any action

n the electrolyte is concerned, copper cathodes. As soon as the copper deposit becomes as thick as cardboard it is stripped off, and these copper sheets are properly hung in the vats to receive a deposit of copper to the thickness desired for the market.

It is hereinbefore shown that the mine waters, or natural solutions, contain H_2SO_4, $CuSO_4$, $FeSO_4$, and maybe, $Fe_2(SO_4)_3$. Electrolysis of such an electrolyte in the apparatus described, results in the deposition on the cathodes of reguline copper, and a solution containing more free H_2SO_4, more $Fe_2(SO_4)_3$ and much less $FeSO_4$. This solution, generally, may be utilized in the treatment of the lower grade ores from the same mine, or near-by ones to produce the artificial solutions, after the manner set forth in describing the treatment in large heaps by water and slow oxidation. This is especially advantageous because such a solution is far more active than water alone in causing and taking part in the decompositions and compositions incident to the process. The sulphuric acid and the ferric sulphate are active in energetically starting the chemical actions, and supplying the needful agents which otherwise are produced so slowly.

Or, if it be desirable, this depleted electrolyte may be used in leaching the ores which have been roasted, and which contain minutely disseminated cupric oxide, and sometimes cuprous sulphide and metallic copper.

The lixiviate running from the leaching tanks into the deposition vats consists of a solution in water of sulphuric acid, cupric sulphate and ferrous sulphate, expressed symbolically as follows:

$$xH_2SO_4 + 2CuSO_4 + 4FeSO_4.$$

The electrolytic action deposits the copper on the cathodes, perhaps by secondary action, without the evolution of hydrogen, but producing at the anode ferric sulphate, as per this equation:

$$x\,H_2SO_4 + 2CuSO_4 + 4FeSO_4 = 2Cu + 2Fe_2(SO_4)_3 + x\,H_2SO_4.$$

Taking the latter half of the above equation for consideration, the two parts of copper are deposited on the cathodes and the solution of ferric sulphate and sulphuric acid runs to the sump tank, from whence it is raised to the stock tank, and from there is used on subsequent lots of powdered and roasted rock in the leaching tanks. While the starting of the plant involves the use of a solution of sulphuric acid for the solvent, all subsequent solvent actions take place in the presence of ferric sulphate and ferrous sulphate as well.

Now, ferric sulphate solutions are energetic solvents of metallic copper, oxides of copper and, to a limited extent, of some sulphides of copper, with reduction from ferric to ferrous solutions and ferric oxide. Take metallic copper and we have this equation:

$$Cu + Fe_2(SO_4)_3 = CuSO_4 + 2FeSO_4.$$

Take cupric oxide:

$$3CuO + Fe_2(SO_4)_3 = 3CuSO_4 + Fe_2O_3.$$

This latter equation shows that ferric oxide (Fe_2O_3) is freed by the solvent action in the leaching tank, and remains there undissolved, thus continually purifying the solution of iron.

The roasting process may sometimes fail to completely oxidize the Cu_2S; if so, then the following equation expresses a further action:

$$Cu_2S + 2Fe_2(SO_4)_3 = 2CuSO_4 + 4FeSO_4 + S.$$

It has been claimed that cupric oxide is dissolved by a solution of ferrous sulphate by double analysis and synthesis, per this equation:

$$CuO + 2FeSO_4 + H_2O = CuSO_4 + (Fe_2O_3 + SO_3) + H_2.$$

The sulphuric acid dissolves some cupric oxide as per this equation:

$$CuO + H_2SO_4 = CuSO_4 + H_2O.$$

It will be seen that all of the reactions result in the production of cupric sulphate in the lixiviate which is to be electrolyzed. There is no deposition of iron on the cathode, even though its sulphate salts are present in the electrolyte in great excess, say near to saturation of the solution.

In the way described, the lixiviate becomes the electrolyte, which, when by electrolysis it has been depleted of its copper, becomes the solvent, for a new cycle of operation in continuity.

The next most important solutions, made in large quantities, are those of gold in a solution of potassium cyanide. These solutions are exceedingly dilute, seldom containing more than ten pounds KCy in a ton, or more than one-half ounce of AuCy. The salt is probably $AuKCy_2$. If this solution be made decidedly alkaline by potash, or soda, when electrolyzed between iron electrodes, with 0.25 volt difference of potential, the Cy set free at the anode is at once appropriated by the alkali to form a cyanide which will act to dissolve gold from the next lot of ore treated with it.

NEW YORK, April 4, 1902.

DISCUSSION.

Mr. C. Hering: In my opinion it is not sufficient to merely give the current density and the concentration. While that may be true, that the proper current density increases with the concentration, such a statement by itself does not lead us to proper results. The best current density depends upon how many molecules can be brought into absolute contact with the electrode; hence it is just as much a function of the circulation as of the concentration. I think more stress should be laid upon this fact, than is usually done. It is not a question of concentration alone; it is a question of bringing the molecules in the solution into immediate contact with the electrode.

Dr. H. S. Carhart: It must not depend upon the ionic velocity alone.

Dr. Keith: No.

Mr. C. J. Reed: In other words, it depends on the presence, at the cathode, of a sufficient quantity of copper to transmit the current, so that nothing else will transmit it and, therefore, there is nothing else deposited except copper.

Mr. A. T. Weightman: Dr. Keith has not given us any particular statement in reference to the cost. He prefers to use lead anodes, and I take it the cell will not require less than two and a half volts. I was working on something similar to this; that is to say, the separation of copper and nickel from a sulphate solution on a large scale, and with lead anodes it required about four volts per cell, a certain amount of hydrogen was also liberated with the copper. At the price Dr. Keith gives for power alone, it will work out nearly four cents per pound for the copper deposited. That seems abnormally high and compares unfavorably with precipitation by iron.

Mr. Titus Ulke: There are several refineries that can profitably refine argentiferous copper for about a quarter of a cent a pound. I have good reason to believe that I can produce electrolytic copper from converter bars at Sault Ste. Marie for less than two-tenths of a cent per pound, especially with water-power costing only about $11 per horse-power year for large units.

Dr. Keith: I have had lead anodes in use for nearly two years, and the oxidation of the lead is merely superficial; it does not

seem to penetrate any considerable distance. If the anode is allowed to stand idle in the solution, a local action takes place, it sulphates, and that sulphating is destructive to the anode; the film of sulphate is highly resisting, and, if it is of very considerable thickness, it requires much energy to overcome it, and a long-continued current to decompose and re-oxidize that sulphate back into peroxide of lead. The electrolyte is kept constantly in motion, and the evolution of oxygen which takes place—there is always an excess in that particular—keeps the solution in motion, and the flow of the solution from one tank into the other is so regulated that there is a constant motion. In each cell there is the same number of ions of copper present at the cathode; it is the same in all the cells. That is insured by the variously extended cathode surfaces which are presented. The cathode surface increases directly as the decrease of the copper ions in any given cross section of the solution. The voltage in practice is above one and six-tenths. The counter electromotive force due to the opposition of the electrodes—peroxide of lead anode in one, and of copper in the other—in that particular solution, is one and six-tenths; an expenditure of about one-quarter of a volt serves to overcome all the other resistances and produce the density of current which is necessary.

There is no hydrogen set free. If we should exceed the proper density of current, there would be an evolution of hydrogen and deposition of it upon the cathode to an amount which would preclude the production of reguline copper. We get then a deposition of copper from which hydrogen may be squeezed as from a sponge.

A paper read at the Inaugural Meeting of the American Electrochemical Society, Philadelphia, April 4, 1902, President Richards in the Chair.

A METHOD OF ELECTROLYTIC PRODUCTION OF ZINC FROM ITS ORES.

By Samuel S. Sadtler.

Some little time ago, while experimenting on the electrolytic deposition of zinc from zinc sulphate in the presence of sulphuric acid, I endeavored to find, if possible, a way to deposit zinc more uniformly, free from pits due to the adherence of gas, and also with greater economy of current.

I recalled to mind the electrolysis of double salts of certain metals such as gold, silver, and nickel, as compared with the electrolysis of the simple salts. In these cases the more electropositive metal goes by itself to the cathode and the rest of the molecule passes towards the anode. After this, any action is purely chemical and the precipitation of the heavy metals is due to the action of the cathion upon an unchanged molecule of the double salt.

To make a double salt of zinc, I thought of forming an alkaline zincate compound. This is formed by the action of an alkaline hydrate upon the hydrated oxide of zinc. To carry out this reaction in a practical way, I thought of four classes of preliminary reactions. The first was to form it from the metal, which either meant the action of the alkali upon the metal itself with the evolution of hydrogen or the simultaneous oxidation of the zinc or hydrogen.

The first plan I did not follow, because the zinc has to be in a very fine condition or the solution heated to react to any appreciable extent. To assist the caustic in effecting a solution of the zinc, I then ran over a list of the oxidizing agents which are compatible with an alkaline solution. The only one which would serve this purpose, and could be thought of commercially, which would not hinder the deposition of the metal and which would act in a cyclic way, was an alkaline hypochlorite or hypobromite.

The third reaction or series of reactions was to treat a salt of zinc with such an alkaline oxidizing agent as the hypochlorite

(most particularly the native sulphide of zinc or zinc blende.)

Here the oxidizing agent substitutes oxygen for sulphur of the ore, the sulphur being separated and alkaline zincate being formed.

The fourth reaction was to cause hypochlorite to act upon the elements associated with the zinc, which are not in their highest states of oxidation. The solution oxidizes them, thus breaking up the combination so as to allow the freed zinc oxide in its nascent state to dissolve in the caustic hydrate.

I will speak briefly now, of these last three classes of reactions and some applications for which they might prove useful.

The reaction of the alkaline hypochlorite upon metallic zinc, I have found, applies equally to tin, and if ammonia is used as the alkali, to copper.

In a few words, by this reaction metals, whose oxides in the nascent state are soluble in caustic alkali, may be separated from those whose oxides are insoluble ; thus, zinc, cadmium, silver and chromium and, in certain cases, antimony and copper may be separated from iron, nickel, lead, manganese, cobalt and gold, and gold may be separated from the others last mentioned.

I thought first of scrap tin plate and galvanized iron, and succeeded in leaching off the tin and zinc, leaving the iron unaffected.

There are two difficulties in this operation, the first lies in the fact that the hypochlorite cannot be electrolytically formed as strong as would be desirable to get sufficient metal in solution, so that it could be deposited in good reguline condition. This can be arranged, however, either by arranging the anode compartment or series of anode compartments in such a way that the strong caustic solution runs into the compartment slowly, as it is needed to form hypochlorite with the nascent chlorine, or by charging the solution with the metal at first and throwing out only a certain amount in each cycle, which amount is at once taken up again from the metal in the leaching vessel. The other difficulty is to prevent the formation of oxygen, which would cause dead loss of current. This is best avoided by having a good excess of sodium chloride in the solution, avoiding a large excess of caustic soda, and I believe that higher current density helps the formation of hypochlorite.

The reactions involved are :

To form hypochlorite :

(A) $2NaOH + 2Cl = NaOCl + NaCl + H_2O$.

To dissolve the metal:

(B) $Zn + NaOCl + 2NaOH = Zn(ONa)_2 + NaCl + H_2O$.

In electrolysis:

(C) $Zn(ONa)_2 + 2NaCl + 2H_2O = \overset{-}{Zn} + 2\overset{+}{Cl} + 4NaOH$.

The chlorine liberated in this reaction forms hypochlorite in (A), and the NaCl formed in (A) and (B) gives up Cl in (C), in which it is absorbed by part of the NaOH.

The reactions involving the action of such a solution upon sulphide ores are the same as those on the metals themselves, with the exception that sulphur separates and is deposited in the free state. To act sufficiently, however, the ore must be very fine and for good quantitative results would have to be pulverized in a ball mill and sorted by blowing. For if there is not an excess of sulphide to react, not only the metal but the sulphur is in time dissolved, forming sulphate.

In this process the cycle would be the passage of the hypochlorite solution, formed electrolytically or chemically into the leaching vats containing the pulverized ore. The solution would be formed most cheaply by electrolysis of salt, but if the method of using a concentrated solution of hypochlorite, which I briefly mentioned above, is selected, chlorine gas is passed into concentrated caustic soda solution (about 40 per cent. strength) until half the caustic is used up. In this way a 37 per cent. hypochlorite solution is formed. After acting upon the ore, the solution goes into settling tanks where the sulphur is deposited, from there to the cathode compartments, then to the anode side of the diaphragm, from which it goes back to the ore, thus completing the cycle.

With a current of about 50 amperes per square meter, the voltage would be close to 2.5 (including the drop of potential due to the diaphragm). The diaphragm which seems to be best suited to this solution is one of prepared silicate of alumina.

With regard to the other application of this fundamental reaction, I would mention the action of hypochlorite upon a complex mineral in which the metal desired in solution is already in the oxide condition such as Franklinite. This reaction, I have tried with success in leaching out zinc. The action seems to be that of the oxidizing agent upon the protoxides of iron and manganese and in this way breaking up the combination and freeing the zinc oxide which is at once dissolved in the caustic soda. Here the

expenditure of the oxidizing power of the current may be small for the amount of zinc dissolved, depending upon the proportions of lower oxides of iron and manganese.

I have just touched upon the fact that gold and silver may be separated by this method. They may be not only separated from lead, but may be also separated from each other. This phase of my process is the most hopeful from a commercial standpoint as there would be abundant margins of profits. I have spoken most especially of the recovery of zinc because I first thought of this reaction in that connection. A number of processes such as the Ashcroft and Hoepfner process have been brought out, but as far as I have learned, have failed chiefly because of the difficulties of electrolysis in acid solutions, solution and precipitation of silicic acid and the labor involved. I did believe and still hold that success in electrolytic zinc work is more likely to be reached by the use of alkaline solutions.

DISCUSSION.

Mr. C. Hering: The great trouble in getting zinc out of its solutions is that the solvents of the zinc which are generally present, are usually more easily decomposed than the zinc compound itself. For instance, in electrolyzing zinc sulphate, if there is any acid present at all, the current will prefer to decompose that acid rather than the zinc sulphate. That is the reason it is so hard to get the zinc out of that solution; I think this fact will interfere in most processes of extraction. The only way to prevent this undesired decomposition is either to use some solvent which would not decompose at the required voltage (if such a solvent exists), or else to have no excess of the solvent.

Mr. Sadtler: I haven't measured the amount of zinc deposited, but have judged the efficiency by the liberation of gas and regeneration of the solution. I made a number of reactions qualitatively before I made quantitative tests.

Dr. N. S. Keith: I have, in practice, deposited a great many hundreds of pounds of tin in separating tin from tin scrap by the use of alkaline solutions, using a stannate, for instance of soda, in the presence of chloride of sodium. A hot solution containing stannate of soda and chloride of sodium will act to dissolve tin at

the anode, and the tin will be deposited in a beautiful crystalline form; and while the solution is boiling there is no action whatever upon the iron; there is no more deposition of tin than there is dissolved, and the solution is quite permanent; nothing but water need be added. It seems to me, in this line zinc might be treated using zincates in place of stannates.

Mr. P. G. Salom: I have worked a little in the reduction of zinc directly from the zinc blende. But I found the same difficulty that Mr. Hering found: that the amount of current required was very much higher than the theory called for. Of course, I knew what the cause of that was, but I have never gone far enough in the matter to see how it can be avoided. I have been able to produce a pound of zinc with about four horse-power hours, and I have produced quite considerable quantities in that way in the laboratory—not more than a few pounds altogether, I suppose—but enough to get quite large amounts of zinc sponge, and then press it up the same way we do the lead sponge.

Mr. Sadtler: I think the current efficiency is a little better in the chlorine solution than it is in the lead solution. I haven't any accurate figures at hand as to the voltage of decomposition, that is, of some of those complex salts, but the voltage of decomposition of this was several tenths of a volt different from any of the soda solutions. I was very much surprised I had got my zinc down at a lower voltage in the zinc solution than I had in the alkaline solution.

Mr. Hering: I do not know whether the voltage of decomposition of alkali is considerably below that for zinc. In the case of the acid solution the discrepancy is quite great; the voltage for decomposing the acid is about 1.4 while that for the zinc sulphate is about 2.3. I have obtained a current efficiency of 95 per cent. in a zinc process, but that was by having absolutely no acid in the solution.

Mr. P. G. Salom: Mr. Chairman, I would like to ask Mr. Sadtler what current efficiency he can count on—how much per pound?

President Richards: I think Mr. Hering's remarks will apply to zinc salts where there was free acid present, and by separating hydrogen you have that inefficiency,—in the case of zinc sulphates. In solutions of sodium zincate I would suppose the zinc is set free

by the secondary action of liberated sodium in the same way as the liberation of gold from the gold cyanide.

Mr. Hering: It takes a still higher voltage to separate sodium.

President Richards: In electrolyzing sodium zincate, sodium itself is the cathion, and replaces zinc from the solution by secondary action; and the sodium being then the agent which produces zinc, the problem of how much hydrogen it would form simultaneously, would be a more difficult question, perhaps, than the question of how much hydrogen there would be produced from the electrolyte itself by electrolysis.

Mr. Hering: I have worked out the calculations and I find they amount to the same thing, whether you deposit zinc directly or have the sodium deposit the zinc.

Mr. Sadtler: I spoke of keeping down the presence of excessive amounts of caustic soda and raising the percentage of salt for the action on the anode as well as on the cathode, and of course all those things have to be taken into consideration in getting the efficiency.

A paper read at the Inaugural Meeting of the American Electrochemical Society, Philadelphia, April 4, 1902, President Richards in the Chair.

THE ELECTROLYTIC RECTIFIER.

By C. F. Burgess and Carl Hambuechen.

The facility with which the alternating current lends itself to voltage transformation is making this form of current the standard for electric power transmission purposes. This condition together with the difficulty of applying the alternating current directly for certain purposes such as series arc lighting and traction work, and the impossibility of employing it for electrolytic work, including the charging of storage cells, makes the transformation of an alternating into a direct current an operation of increasing importance.

That this problem has not received a satisfactory solution is evidenced by the disadvantages attendant upon existing commercial means of obtaining unidirectional current from alternating current lines. The synchronous rectifier or revolving reversing switch, while of considerable simplicity and high efficiency, has the apparently insuperable disadvantage that adjustment for minimum sparking is almost impossible to attain on account of the varying relation between inductance and capacity on the line. With rotary converters we have among other disadvantages the low weight and energy efficiencies, especially with smaller sizes, and the great cost.

The equivalent of the static pressure transformer which is used on alternating circuits would be an ideal solution of this problem, and among various devices having no moving parts which have been suggested, the electrolytic rectifier gives the greatest promise of commercial success.

From some of the claims which have in the past been made for the electrolytic rectifier we are led to doubt the justification of such claims or to wonder why apparatus embodying them has not begun to replace the more expensive, less efficient, more cumbrous methods of common practice. Such condition justifies the statement of the practical man that the utilization of the electro-

lytic cell as a rectifier possesses considerably more interest than value.

To determine if possible the practicability of successfully utilizing the electrolytic cell for this purpose the writers undertook an experimental investigation, some of the results and conclusions of which are here given. Attention was confined largely to the utilization of that remarkable property which various metals, particularly aluminum, possess in certain electrolytes of allowing current to flow freely in one direction and offering great resistance to its flow in the opposite direction. This phenomenon, which seems to have been first discovered in 1855 by Wheatstone, has been the basis of a considerable amount of speculation and of experimental investigation ever since. The commonly accepted view is that aluminum by means of its property of being easily oxidized (this term being used in its general sense) in certain electrolytes becomes so thoroughly covered with a continuous oxide coating that it effectively insulates the plate from the surrounding electrolyte and prevents any flow of current as long as this coating is maintained. When the pressure is in such direction as to make the aluminum the anode the effect is to maintain this insulating coating unless the pressure be high enough for disruption. When the aluminum is the cathode this insulating coating offers little or no barrier to the flow.

A question which is suggested by the above explanation is, if the insulating coating prevents the flow of current in one direction why is it not an insulator for the opposite direction? Further, the protective coating of the aluminum plate is formed at the expense of a certain amount of corrosion of aluminum by oxidation and this coating is destroyed or removed when current flows toward the plate, which must be done without the redeposition of aluminum, for as far as is known this cannot be done from aqueous solutions. The aluminum coating must be of a certain appreciable thickness to prevent flow of current and if this coating is formed and destroyed 60 times a second it ought not to take long before the aluminum plate is completely oxidized, which is found to be contrary to fact. Observations which were made lead to the following conclusion upon these points. The coating on the aluminum does not absolutely insulate but offers a resistance so high that only a small current (sometimes immeasurably so) flows when the aluminum is the anode. The

leakage current does not flow uniformly from the surface but only from portions of it having lowest resistance and thinnest coatings. These portions are small openings or points distributed somewhat irregularly over the surface and the current flowing through these points produces enough heat to give the well-known sparking effect if pressure is sufficiently high. On reversing the direction of the pressure the current flows through these small openings and in so doing enlarges them, the resistance being thereby greatly decreased. On again reversing, this opening is immediately closed or contracted, which process may be considered as continuing at a rate equal to the frequency employed. The sparking seems to be the result of the leakage current, and from the general appearance of the sparks the amount of leakage may be estimated. When sparking is sharp, bright, distinct and occurring in fine sparks, the leakage is of a low value, and where sparks are larger and duller and in the nature of flashes, the leakage is greater.

The entire surface of the aluminum then does not act as the active electrode, but only those parts upon it at which the sparking or leakage takes place. It is undoubtedly the case that the expansion and contraction of the openings which takes place at these discharge points is due to the formation and destruction of the aluminum oxide coating, and, as before indicated, results in the continual oxidation of aluminum. This oxidation or wearing away does not, however, occur uniformly over the entire surface, but only at those localities (constituting a small proportion of the surface) at which the sparking occurs. This results in a gradual wearing away at these points, as evidenced by the marked pitting of the electrodes which may be observed after a considerable length of time of operation.

Some idea of the relative proportion of an aluminum surface which is active in a rectifier consisting of aluminum and lead electrodes in a potassium phosphate solution may be obtained from Fig. 1. This is a photograph of an aluminum electrode magnified 21 diameters, which had been in operation on an alternating pressure and which was subsequently immersed as cathode in a copper sulphate solution and a current of low density caused to flow. This produced a deposit of copper at various points on the aluminum surface not protected by the insulating coating, or, in other words, the spots showing the copper deposition indicate

the position of the electrolytic valves. By taking a similar aluminum electrode and causing it to receive a very low current density as cathode in the phosphate solution for one-half minute, and then repeating the copper deposition process, the active surface is seen to be greatly increased. This is shown by Fig. 2, and bears evidence to the statement that the electrolytic valves consist of openings in the protective coating which expand and contract, according to the direction of the flow of current.

Reports of efficiency for the electrolytic rectifier have appeared in engineering and scientific publications from time to time, giving values of current and energy transformations of 90 and even 95 per cent., but such claims appear to have been made without considering all the factors or the conditions which have to be met in practice. Estimates for efficiency have been based upon the single factor, *internal resistance* of the apparatus. The statement that an aluminum rectifier "will give an efficiency of 95 per cent. provided the electrodes be made large enough," assumes erroneously that the direct heating effect of the current flowing through the resistance is the only loss in the cell.

The losses in the rectifier may be divided as follows : C^2R loss, C being the current flowing toward the aluminum and R being the resistance of the electrodes and electrolyte.

CE', where C is the current flowing toward the aluminum electrodes and E' is the counter electromotive force which is developed by the decomposition of the electrolyte.

$C'E$ where C is the leakage current flowing from the aluminum to electrolyte and E is the applied pressure.

The direct heating effect of the current while flowing in the useful direction may be made as small as desirable by decreasing the current density and by placing the electrodes in close proximity. The former is limited only by convenience of size and the cost of cell for given output, and the latter by mechanical construction consistent with freedom of circulation and the avoidance of short circuits. If this loss were the only one to consider, the question of efficiency of electrolytic rectification would be practically solved. An electrolyte having a resistance as low as ten ohms per cubic centimeter can be readily obtained, and with such electrolyte and with electrodes one centimeter apart, the resistance of a cell per square decimeter would be one-tenth of an ohm. This would produce, with a current density of 5 amperes,

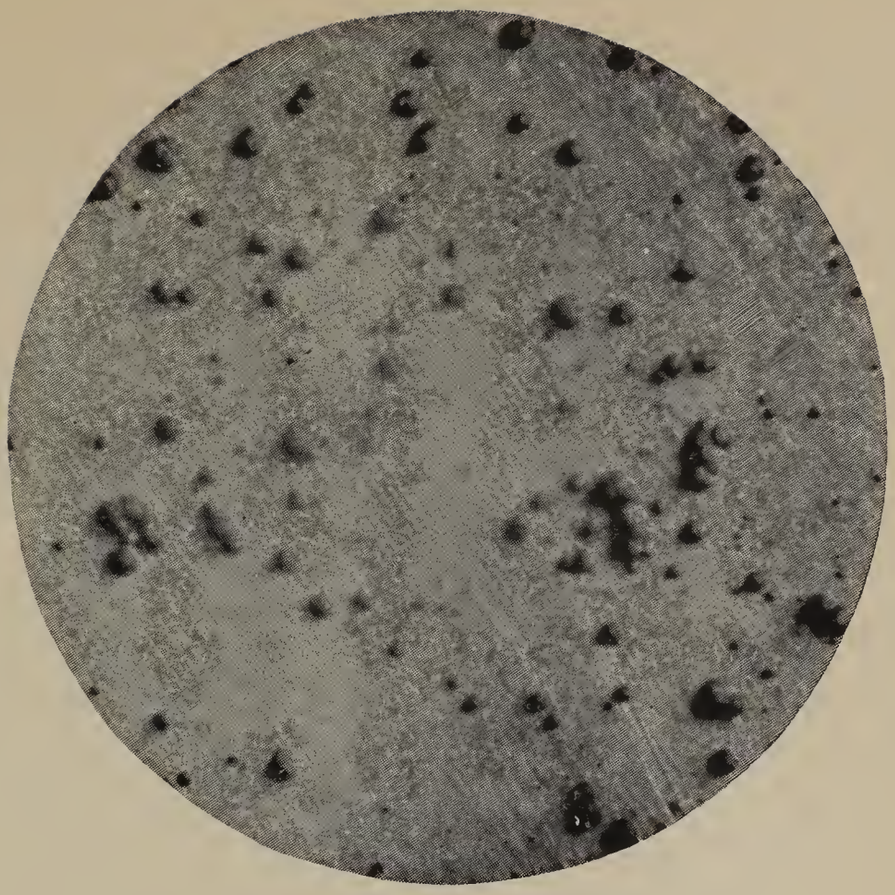


FIG. 1.

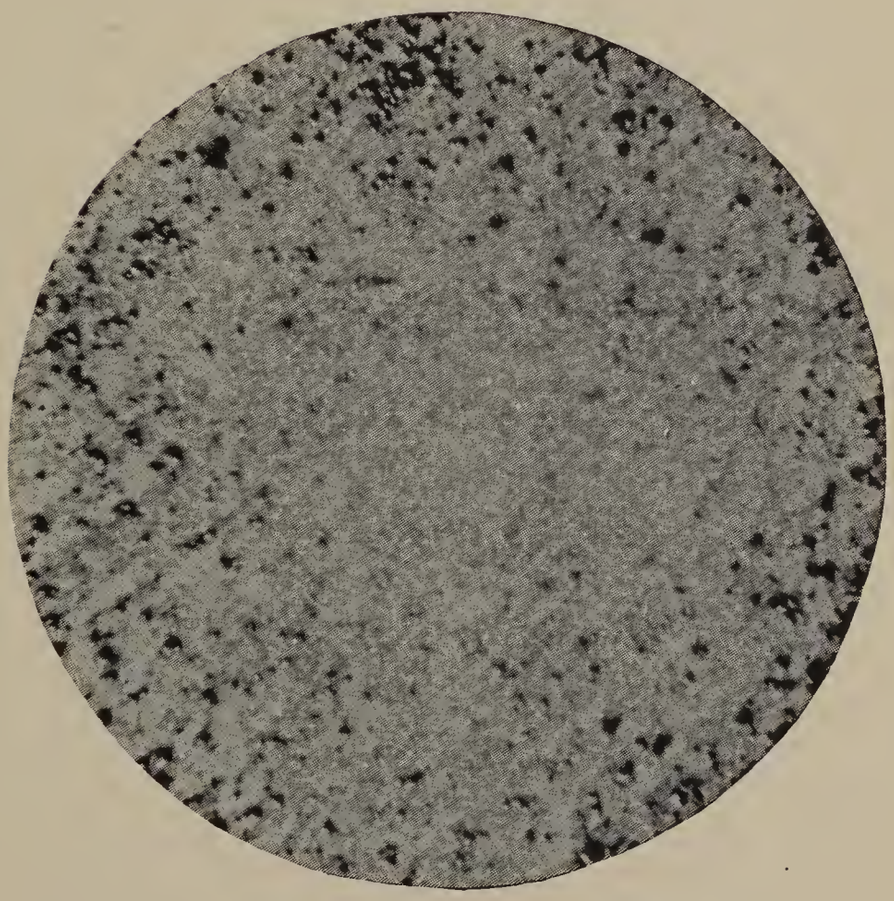


FIG. 2.

a drop of only one-half volt which, with an applied pressure of 25 volts, would mean a loss of 2 per cent.

It should be borne in mind, however, that the resistance of the electrolytic cell cannot be accurately figured from the specific resistance and the volume of the electrolyte inasmuch as only a small proportion of the aluminum plate is an active electrode surface and the resistance between the electrodes may, therefore, have a much higher value than calculations will show. The internal resistance is a variable quantity, being least when maximum current has flowed toward the aluminum and greatest after the maximum pressure has been applied with aluminum as the anode. The fact that the reduced area of the active aluminum surface has the effect of reducing the cross-section of the electrolyte was shown by measuring the resistance of an electrolyte with an aluminum cathode, and again with a carbon cathode. In the latter case the resistance was found to be 2.5 ohms as against 5.5 ohms in the former. This resistance of the electrolyte is not reduced proportionally as the electrodes are brought nearer together inasmuch as the greater part of the resistance exists near the aluminum electrode.

The current flowing through the electrolyte causes decomposition which cannot be avoided, inasmuch as most of the current flows in one direction. This, of course, requires a certain amount of energy, depending upon the current passing and the counter electromotive force. The counter electromotive force within the cell has a value depending upon the electrolyte and the electrodes. If the anode be a corrodible metal this pressure may be lower than where an insoluble metal, such as platinum, is used, but this lowering of counter electromotive force would be at the expense of corrosion of the electrode, which would probably be undesirable for commercial purposes. E' may have a value varying from 1 to 3 or 4 volts. This loss of energy shows itself primarily by a change of the composition of the electrolyte, and if the substances produced thereby recombine within the electrolyte, heat is produced. For a commercial rectifier the electrolyte should be so chosen that it produces a minimum pressure of decomposition and it should be sufficiently cheap that the waste of material by decomposition is a small amount. To reduce this source of expense to a minimum

it may be desirable to construct the cell so that the liberated materials will recombine as completely as possible. The decomposition of the electrolyte, which cannot be avoided, offers the possibility of being the source of profit rather than expense if the products of decomposition are of greater value than the original material and provided they can be collected economically. This, however, from the commercial standpoint is a possibility rather than a probability.

The fact that a portion of the current flows in the wrong direction is probably the greater source of the difficulty with the electrolytic rectifier, and it is upon limitation of this leakage that commercial success depends. The leakage current may be made visible by the brilliant sparking which occurs over the surface of the aluminum, and it is evident that the energy thus expended, which may be of very considerable amount, is concentrated almost entirely upon the aluminum surface and manifests itself in the form of heat.

It will be observed that nearly all losses cause a liberation of heat, which tends to raise the temperature of the apparatus to such a point that it breaks down or becomes inefficient. The output of the apparatus is, therefore, limited to the rate at which the heat may be dissipated and to the maximum temperature allowable ; a large output means small losses, method of cooling, and a high allowable temperature.

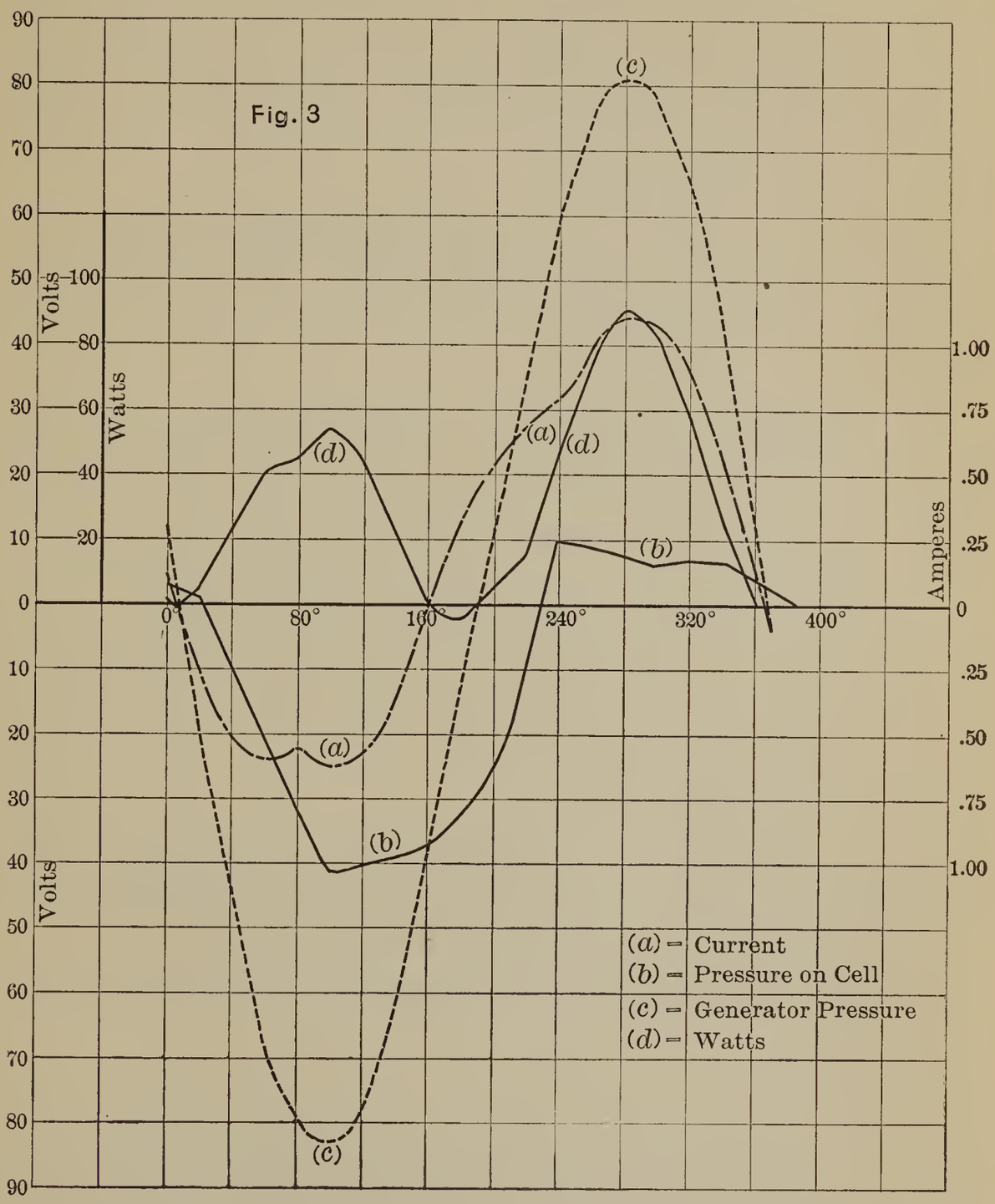
To find the relations between these losses, a number of tests were made under various conditions, the results of some of which are here given. The method of studying the problem was by means of current and pressure curves obtained with an instantaneous contact maker.

The curves on Fig. 3 show something of the operation of an arrangement consisting of an electrolyte of potassium phosphate having a density of 1.27 sp. gr. and slightly acidified, in which were placed an aluminum sheet electrode having an immersed area of 45.5 square inches and a lead electrode of similar size. The aluminum electrode was previously cleaned and immersed for some time in a sodium hydroxide solution and then "formed" in the phosphate solution by applying a pressure from a direct current circuit with the aluminum as the anode.

The cell was then connected in series with a non-inductive resistance to the brushes of an alternator, and current and pressure

curves were obtained. The method of connection is shown in Fig. 4.

The portion of the current curve (*a*), Fig. 3, below the base



line indicates the current which flows from the aluminum plate to the electrolyte, or the leakage current, and the remainder of the curve shows the current in desired direction. The pressure curve across the rectifying cell is shown by curve (*b*), the negative part being the pressure at which the leakage current flows through the cell and the positive part representing the CR + E′ in the cell where C is current flowing, R is internal resistance,

and E′ is the counter electromotive force of polarization. The pressure applied to the circuit by the generator is indicated by the sine curve (*c*).

It is to be noted from these curves that there is a very considerable leakage current: the loss due to CR + E′ is seen to be much smaller than that due to leakage. The current curve being in advance of the pressure at the center of the cycle shows that there is some capacity effect.

The curve (*d*) showing the watts delivered to the circuit gives an idea as to the loss due to leakage as compared with the watts delivered during the remainder of the cycle. The average watts delivered to the circuit is 33.9. The average watts lost in leakage is 13.9.

In making the above tests we attempted to use the solution and electrodes as recommended by Pollak,[1] following his description as closely as possible in setting up the cell. The best efficiency, however, which we succeeded in attaining was so low as to lead to the belief that some essentail detail was omitted in the published descriptions or that errors in interpreting the same were made by us. The efficiency here shown is not sufficient to guarantee any extended commercial applications, and especially so as the electrolyte must be kept below 40° C., which means low size and weight output.

The leakage seems to be the principal subject for study in bringing the electrolytic rectifier to commercial efficiency. The leakage depends upon various factors including the following:

Electrolyte—as to composition and temperature.

Aluminum electrode—as to composition and surface exposed.

Pressure.

Frequency.

That the proper choice of electrolyte is important is shown by the fact that comparatively few substances will give satisfactory results. Among electrolytes which have been proposed are aqueous solutions of sulphuric acid, sodium and potassium phosphate, sodium potassium tartrate, and alum.

The temperature plays an important part as shown by the fact that if the temperature rises beyond a certain point low efficiency or complete failure of the cell results. Pollak gives 40° C. as the maximum allowable rise of temperature for potassium phosphate solution.

[1]Bulletin Soc. Int. Electric, July, 1901. Paper by M. J. Blondin.

The leakage seems to depend upon, if not actually proportional to, the area of the aluminum surface immersed in the electrolyte and this being the case we are led to the use of high current densities. This is antagonistic to reducing the C^2R loss to a minimum which requires as low a current density as possible. A suitable balance between these two losses will have to be determined upon. It has been our observation that when the alumi-

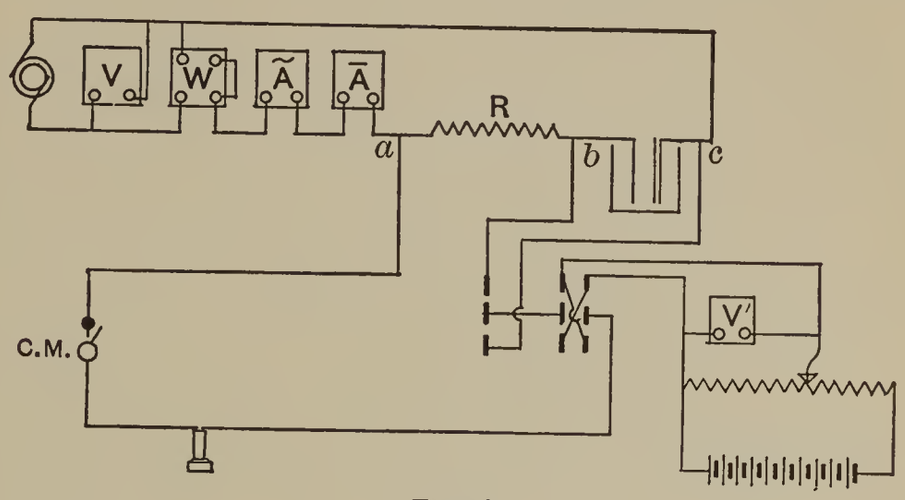


Fig. 4

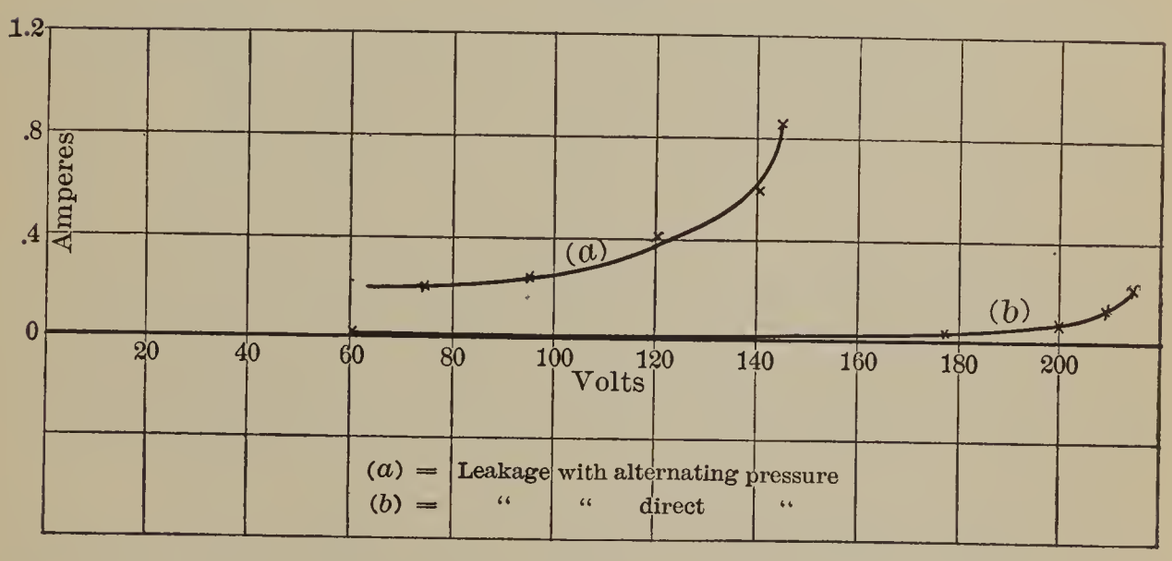


Fig. 5

num electrode becomes grooved or pitted by continued action of the current the leakage increases, due probably to increased area of surface, and smoothing down by hammering or polishing or grinding will increase the efficiency of such electrodes.

The purity of the aluminum will have some considerable influence upon the leakage, inasmuch as the presence of another metal either as an alloy or in metallic contact reduces or destroys the rectifying action of the aluminum. It is possible, however, that some alloy of aluminum may be discovered which will have

a more efficient action than does pure aluminum. The writers found that a small amount of chromium in the aluminum appeared to give it some slight advantage in efficiency, in addition to making it somewhat harder and more durable than the pure aluminum.

That leakage will depend upon the pressure applied is evident upon taking the characteristic of a cell having two aluminum electrodes, using either direct or alternating pressures. The leakage increases proportionally with the pressure to a certain point when the rate of increase becomes much greater. This is shown in Fig. 5 where curve (*a*) is for two aluminum electrodes in a sodium potassium tartrate solution using an alternating pressure, and curve (*b*) is for the same plates with unidirectional pressure. It will be seen from these curves that the behavior on alternating and on direct current circuits is very different and that the amount of leakage in one case is not a direct indication of the amount of leakage in the other. An aluminum electrode may successfully withstand 200 volts unidirectional pressure and not operate successfully on 120 volts alternating pressure. It will also be noted that with direct pressure up to 150 volts the leakage was almost a negligible amount, while with an alternating pressure of 75 volts the leakage was many times greater. This difference was probably due, at least, to a considerable extent, to the condenser effect which the aluminum electrode shows, allowing a capacity current to flow with the alternating pressure.

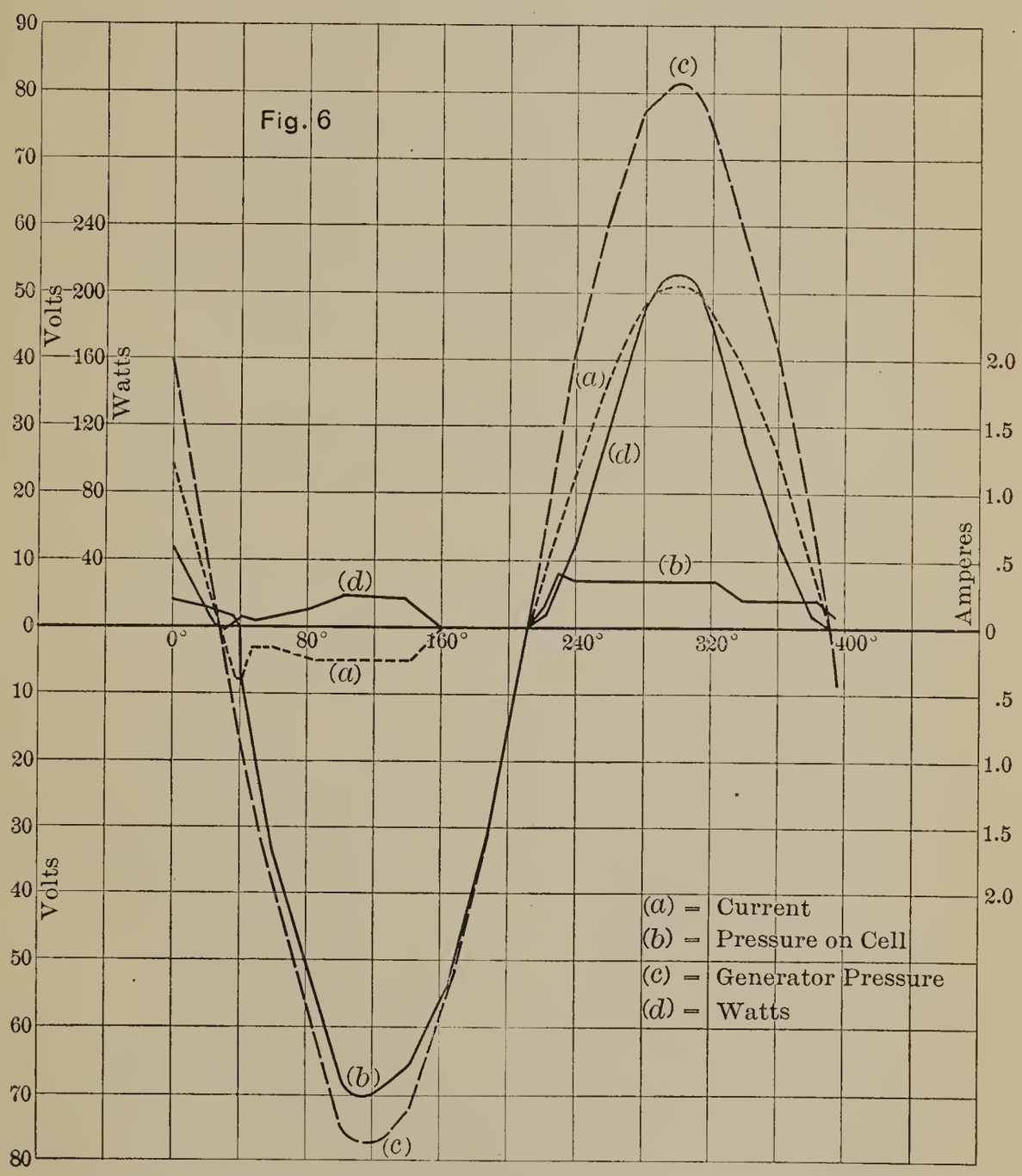
The sparking which occurs in both cases had very much the same appearance but there was this difference to be noted, that with equal values of leakage of the current, the sparking with the direct current seemed to be more violent than with the alternating.

It will thus be seen that no exact conclusions as to the action of the aluminum electrodes on alternating pressures can be drawn from observations made with unidirectional pressure as some experiments have evidently assumed.

The influence of frequency upon the leakage and the efficiency of the electrolytic rectifier is a question in regard to which we are unable to draw definite conclusions although a number of tests were made for the purpose of determining this point. Frequencies from 7 to 125 per second were used and in some cases higher efficiency was obtained with higher frequencies and in some cases the reverse condition held. The difference,

however, was slight with the frequencies worked upon which represents the range of present practice and the conclusion may safely be made that the question of frequency is one of minor importance as far as efficiency is concerned. This is a subject, however, deserving of further investigation.

The frequency may, however, have an important influence



upon the condenser action of the rectifier in producing a low power factor. To reduce this capacity effect, the remedy is evidently a decrease of the aluminum surface or an increase in current density.

For the purpose of increasing the efficiency of operation we have used a large number of electrolytes, but with indifferent re-

sults until the idea of using a fused electrolyte presented itself. Certain molten salts gave such decided improvement in results that extensive investigation was made in this field, and from a great many curves taken, Fig. 6 gives some typical results, such being obtained by use of an aluminum and an iron electrode in molten sodium nitrate.

Curve (*a*) represents instantaneous valves of current, the negative values indicating leakage. Curve (*b*) gives values of pressure at terminals of rectifier and curve (*c*) shows form of pressure wave delivered by the alternator at a frequency of 58. These curves compared with those of Fig. 3 and obtained under similar conditions as to pressure, frequency, and output show decided differences in operation between aqueous and fused electrolytes. The leakage is seen to be a much smaller percentage of the total current flowing.

The loss due to internal resistance and counter pressure is smaller in spite of the fact that the aluminum electrode in the fused salt was about one-fortieth the area of the aluminum in the aqueous solution.

The portion of the curve (*a*) between 30° and 50° demonstrates, we believe for the first time, the interesting fact that at the instant of reversal of aluminum from cathode to anode it offers little resistance to the flow of current, but that it quickly recovers itself and closes the current valve. The rapidity with which this action takes place is seen to be somewhere in the neighborhood of $^1/_{1100}$ of a second at the beginning of a sine pressure wave. After applied pressure has reached its maximum negative value the leakage current rapidly decreases to nearly zero where it remains until reversal of applied pressure again takes place.

The rapid increase, and slight elevation of curve (*b*) at the point 230° shows that the "formed" aluminum plate offers considerable resistance to the flow of current toward it but the resistance almost instantly diminishes. The portion of curve (*b*) from 340° to 400° consists mainly of the counter pressure which maintains its value even after direction of applied pressure has changed as shown by the fact that (*b*) becomes negative *after* (*a*) has reversed in direction.

A further observation is the fact that there is no evidence of capacity effect or difference of phase between pressure and cur-

rent, which is so noticeable in curves in Fig. 3. This is undoubtedly due to the much smaller area of the electrode surface acting as condenser plates.

Curve (*d*) shows instantaneous values of watts delivered to the circuit, the portion from 30° to 160° representing the loss due to the leakage and from 200° to 380° the watts delivered during remainder of cycle. This curve shows an energy efficiency of over 80 per cent.

It will be observed that at a point at about 40° the value of the watts is negative to a very slight extent indicating that energy is being restored to the circuit. This is undoubtedly caused by the aluminum plate acting in conjunction with the iron as a voltaic cell, delivering energy at the expense of corrosion of aluminum. This delivery of energy, however, at the expense of the aluminum continues only for a very short part of the cycle, or until the "valves" begin to work. While having no figures to demonstrate this fact it seems reasonable to suppose that the small amount of corrosion of aluminum which takes place when used in a rectifier is due to, and proportional to, this energy delivered to the circuit.

Among the advantages which may be claimed for the fused electrolytes in comparison with aqueous solutions in addition to sharper and more clearly defined action, higher efficiency, and low inductive capacity effect, are large output per unit weight of cell, which is attained through ability of the cell to stand a high temperature in addition to the much greater conductivity which a fused salt may show over an aqueous electrolyte.

A difficulty in carrying on an experimental investigation upon electrolytic rectification is in the uncertain error which is introduced by the use of ordinary electrical measuring instruments. The amount of error depends upon the type of instrument used and form of current or pressure curve. A complete investigation of the subject of measuring interrupted, fluctuating or pulsating currents was not attempted, but a number of observations will show something of the order of the errors which may be expected.

A circuit carrying a current of the form indicated by curve (*a*), Fig. 6, had in series, three amperemeters of various types together with a copper voltameter. The three instruments represented the hot wire type, the Hoyt alternating current and the Weston direct current type. It was assumed that the voltameter

would give a correct indication of the amount of current rectification and upon that supposition the Weston instrument gave a reading of 94 per cent. of correct value, or 6 per cent. low. The hot wire instrument gave a value 55 per cent. high, and the Hoyt instrument was 64 per cent. high. Using a combination of rectifying cells so as to obtain a pulsating current which did not reverse during any part of the cycle it was found that the Weston instrument still indicated too low a value by $5^1/_2$ per cent. ; the hot wire instrument was 17 per cent. high and the Hoyt instrument 23 per cent. high.

One of the chief uses mentioned for the electrolytic rectifier is the charging of storage cells, and the question will naturally arise as to whether the form of current which is furnished to the battery will be advantageous or disadvantageous to it. Mr. A. B. Marvin, who has been conducting extensive storage battery tests in the electrochemistry laboratories of the University of Wisconsin, took up the investigation of this question. A number of tests consisted in comparing the capacity and efficiency of the storage battery when charged from a steady, and from a pulsating or rectified current. Two storage cells were repeatedly charged and discharged under normal conditions and with steady charging current with the object of ascertaining as accurately as possible the capacity and efficiency of the cells. A rectified current was then substituted for the steady one in charging, and the capacity as shown by the discharge together with the efficiency was in all cases almost identical with the values obtained with the steady current. These tests seemed to show almost conclusively that the pulsating current, even if it has not a marked beneficial action upon the cell, as some writers claim, at least has no harmful action.

The question as to the influence of a pulsating current upon the character of electro-deposited metals or for other electrolytic purposes, is a subject which appears worthy of investigation and might lead to some new commercial applications of the same.

From the results of our investigations the possibility of commercial development of electrolytic rectification seems promising. With the present known means of rectifying with an efficiency of over 80 per cent. competition with the rotary converter, especially in the smaller sizes, is in favor of the electrolytic rectifier while in weight and cost, the balance is very decidedly in its favor.

We have no reason for assuming that further discoveries and improvements will not be made in the electrolytic rectifier and its application to practical use, and with such development its importance would proportionally increase. It may be possible to discover a better electrode than is furnished by pure aluminum, as regards leakage and maximum pressure at which it will operate. That we are not limited to aluminum as the active electrode has been shown by the same phenomena which some of the common metals, such as lead and copper, may show under proper conditions of electrolyte and current density. Lead in concentrated sulphuric acid into which a small amount of sodium bichromate had been dissolved was made to show an interrupting effect, a pressure of 65 volts having been opposed.

Similar possibilities are open for the discovery of new and improved electrolytes. We are not limited to fused or aqueous liquids but may be able to find advantages in the use of solutions in organic solvents.

The form of current obtained by use of a single pair of electrodes, as shown in curves in Figs. 3 and 6, is not suitable for most commercial purposes. The large degree of fluctuation and the slight reversal in direction would be disadvantageous on the operation of motors, and while storage batteries placed on such circuit become charged, the efficiency would not be high inasmuch as the pressure of the cells is added to the pressure applied to increase the amount of leakage. The commercial rectified current should always be in one direction and as near a steady current as possible. There are various combinations of cells and apparatus to accomplish this result but it is not the purpose of this paper to take up this branch of the question. As an illustration of one method for accomplishing this may be mentioned the well-known Pollak and Graetz method of joining four cells in such a way as to give a current which flows continually in one direction though of pulsating value. We deem it undesirable to present at this time the arrangements and devices for accomplishing similar results on account of protection which is expected from the Patent Office. We hope, however, to be able to present a description of such methods and improvements before this Society at a future date.

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UNIVERSITY OF WISCONSIN,
MADISON, WISCONSIN.

DISCUSSION.

Mr. E. A. Sperry: Mr. Chairman, I have done considerable work in attempting to adapt the ordinary aluminum rectifier to practical service without success. It is not a commercial apparatus, at all. In a few hours it breaks down, and its efficiency as has been stated by Mr. Steinmetz is only about 20 per cent. when working at its best. As to the comparative results obtained in charging a storage battery by interrupted current, I might say that using a mechanical interrupter or rectifier, such as a synchronous motor working a turbine interrupter, giving off only a pulsating current cutting the tops of the waves with intervening spaces of rest, and measuring the energy through an ordinary Thomson watt-meter, we have data to show that a battery gives higher efficiency when so charged, this being somewhat different from the statements made by the reader. This might be explained by the indifferent action of the watt-meter itself; there, however, being no iron present in the watt-meter, I see no reason why a pulsating current of the kind described, especially of as low frequency as sixty cycles, would interfere in the slightest with its accuracy. The results that I speak of were repeated in different hands, and I think they are reliable. They showed an advantage of somewhere near 9 per cent.—not a very large percentage, but decidedly on the right side.

Mr. C. Hering: I would like to add my admiration of the excellent work of Professor Burgess and the results obtained by him.

Dr. H. S. Carhart: I notice in the first electrolyte the size of the voltage is very much smaller than in the other. That would account for the smaller watt capacity.

Professor Burgess: I would like to say I am not responsible for the discovery of the value of fused salts in rectification. Any credit which may be given for the same is due to my assistant, Mr. Hambuechen, who is the discoverer of this property. We subsequently carried on the experimental and development work together.

In regard to measuring the rectified current by means of ampere meters, we found that meters of various types gave various errors.

In checking such instruments with the copper voltameter we found that errors of 10 per cent. might always be expected. Similar errors were also found with watt-meters. Measurements of the efficiency of such current in charging a storage cell were made by the use of voltameters, and we have been unable to find much advantage in the use of pulsating over steady currents for this purpose.

PRESIDENT RICHARDS: I would like to ask how you would determine the watt efficiency by the copper voltameter.

PROFESSOR BURGESS: This may be done by using two voltameters, one for determining the current passing into the storage cells, and the other, connected in series with a non-inductive resistance of known value, for determining the pressure.

A paper read at the Inaugural Meeting of the American Electrochemical Society, Philadelphia, April 4, 1902, President Richards in the Chair.

CAUSTIC ALKALIES AND CHLORINE BY THE DRY ELECTROLYTIC PROCESS.

By C. E. Acker.

The experimental work in connection with the development of the present fused bath process for the manufacture of caustic alkalies and chlorine began in 1894, at which time an experimental plant was built near the Courtland Street ferry in Jersey City for the purpose.

The general object at that time was to develop methods for electrolytically decomposing fused salts, such as sodium chloride and other allied salts, which were fusible at moderate temperatures, and to obtain the metals themselves or any compounds of the metals which might be produced advantageously.

The author had previously devoted considerable time to the study of aqueous bath or wet processes, and had built several different types of cells for decomposing brine, the current which was available for this purpose being 350 amperes.

The literature relating to the subject of electrolysis of solutions was somewhat extensive, and a large number of patents had been issued in various countries covering numerous processes, forms of cells and particular features relating thereto, and these were all available for examination. There was not much published information to be had relating to the electrolysis of molten compounds, and such as could be found was not particularly encouraging.

The first extensive experiments and the first publication relating to the electrolysis of molten sodium chloride were due to Professor A. J. Rogers, of Milwaukee. The first United States patent relating to the electrolysis of molten sodium chloride was applied for by Professor Rogers, in April, 1883, issued and published in 1884. It will thus be seen that Professor Rogers was an early worker in this field. His experiments in the electrolysis

of molten compounds were continued for many years. We find the results of some of his work recorded in periodicals in 1889–'90, '94, etc., both here and abroad, the publication of which has been of service to several workers in this field.

While it had long been known that lead and sodium would form an alloy, Professor Rogers was the first to make such an alloy in quantity and to note the characteristics thereof, including the rapid decomposition of water, and the formation of caustic soda. He employed lead as the cathode metal in the electrolysis of fused salt for the manufacture of such alloys and used the current from a dynamo for this purpose as long ago as 1888.

He also used other metals, tin, antimony, cadmium, etc., as the cathode metal, and made various alloys with sodium. He mentioned the difficulty of getting materials which would withstand the corrosive action of molten salt and alkali, but at the same time pointed out the very material which is now used successfully for lining apparatus of this character; namely, magnesia. Had magnesia been available to Professor Rogers in the particular form in which it is now employed for this purpose he would have desired nothing better for lining his apparatus.

For the purpose of conducting our experiments we had secured a small three-story factory building in Jersey City and fitted it up with an entirely new steam plant, including Corliss engine and a special separately excited multipolar generator with a current capacity of 1700 amperes, which could be had at any voltage from 5 to 35 volts, making the machine particularly well adapted for experimental purposes. We also installed miscellaneous electrical and chemical apparatus, as well as a very complete workshop, all of which were located on the first floor. The second floor was devoted to storage and the third floor to laboratory and office.

Our first efforts in this plant were directed to the manufacture of rich alloys of lead and sodium in which we were soon more or less successful as far as quantity was concerned, no great difficulties being encountered in producing an alloy containing 10 or 12 per cent. of sodium. The current efficiency of the apparatus was very low, however, and there was considerable action on the linings, and recombination apparently without end. From some published sources we learned that the solution of the difficulty was to be found in discovering some suitable flux or solvent for

use in the bath, which would lower the melting-point of the sodium chloride to such an extent that the operation would proceed smoothly, and without loss. We had occasion afterward to regret that this notion had ever been instilled into our minds for the reason that we followed it up tenaciously and did a great deal of useless work in that line. It had also been pointed out to us in some publications that there were so many difficulties to be encountered in the electrolysis of molten salts as to render any success in this direction almost impossible.

We finally devised a furnace, however, which would continuously produce lead sodium alloy containing 22 to 26 per cent. of sodium, at a fair efficiency, and made many tons of this product. This alloy could be easily converted into caustic soda and sponge lead. A piece of alloy thrown into a bucket of water would decompose the water violently, with the liberation of hydrogen and the formation of a solution of caustic soda, which could be made very strong for a solution.

We desired to make anhydrous caustic soda, however, and this we did by removing the alloy from the furnace, allowing it to cool down to what we thought was a safe temperature, that is, 500° C. or thereabouts, and injecting steam into the mass of the fused alloy. In this way we first produced molten anhydrous caustic soda of a high grade.

The production of the alloy in the furnace was continuous, metallic lead being introduced at one point and the rich alloy being continuously removed at another point. This was made possible only by a peculiar system of mechanical circulation by means of which that part of the alloy nearest the surface was continually skimmed off. In other words, we took the cream of the alloy as it was being formed and isolated it. This alone made it possible to make a rich alloy continuously at a good efficiency, whereas with ordinary methods of circulating or stirring the cathode metal, it had been very difficult to make more than a 10 or 12 per cent. alloy at a low efficiency; concurrently, the other difficulties were eliminated.

Incidentally we made at this time, and before, rich alloys of various other metals, including barium, calcium, strontium, and potassium with lead and also with tin. The metal barium alloys with lead with avidity, as does also calcium.

After succeeding in making rich lead sodium alloy continuously

and in developing the independent apparatus, which we called a converter, for making anhydrous caustic soda directly therefrom, we decided to combine the furnace and converter in one apparatus, and the final result of this combination is the apparatus shown on the screen, which represents an 8000 ampere furnace, such as is now in use at Niagara Falls.

The furnace consists of an irregular shaped cast-iron box with slanting sides on which there is no machine work excepting that required on the terminal where connection is made with the copper bars which carry the current.

The furnace casting is divided into three compartments, one of which is relatively large, is lined with magnesia, or so-called magnesite brick, contains the molten salt and constitutes the decomposing chamber. The bottom of this chamber, *i. e.*, the "hearth" of the furnace is covered with a shallow body of lead, usually about one inch in depth, which also extends into the other chambers through connecting channels. This shallow body of lead on the hearth is caused to move continually in one direction to one end of the decomposing chamber, where it passes through a short channel into one of the small chambers called the "well." From this small chamber it is elevated and forced over a dividing wall or partition into the adjoining small chamber called the "caustic chamber," from which the lead passes into and through a long channel to the other end of the furnace casting where it again spreads over the hearth and comes in contact with the salt.

The circulation of the lead is effected by means of an apparatus somewhat analogous to a steam injector, which consists of a vertical cast iron tube, called a converter pipe, the lower end extending into the lead contained in the well, the upper end of which is attached to a deflector, which serves also to cover the well, and the caustic chamber.

The steam is introduced through a steel pipe having thick walls and a small bore, the end of which is made of nickel steel and contains a small orifice through which the steam escapes. The steam pressure employed is about forty pounds per square inch.

The jet of steam directed upwardly through the converter pipe carries the mass of lead forcibly through the pipe, which strikes against the deflector cover and falls back into the caustic chamber and thence to the other end of the furnace.

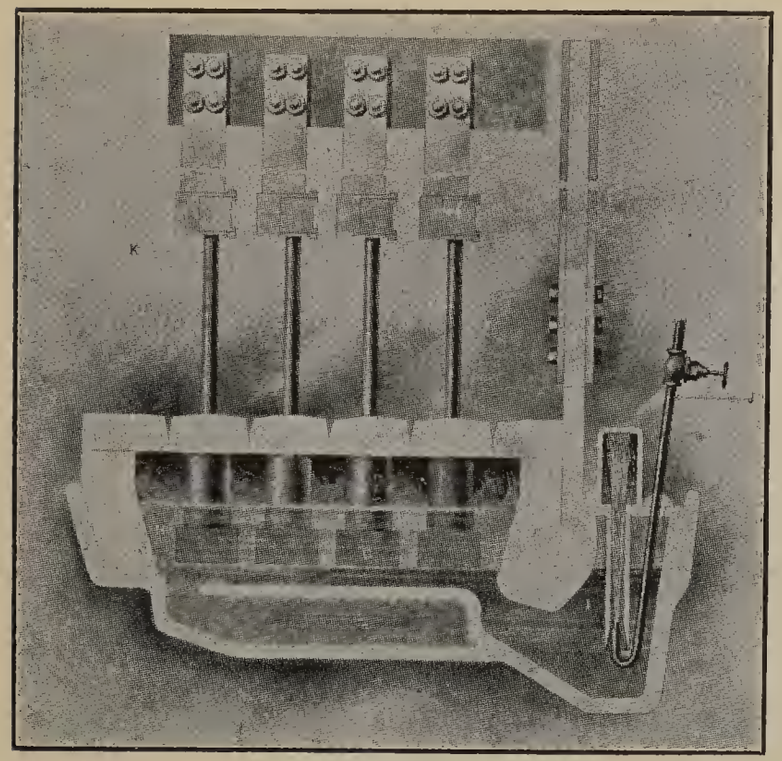

FIG. 1.

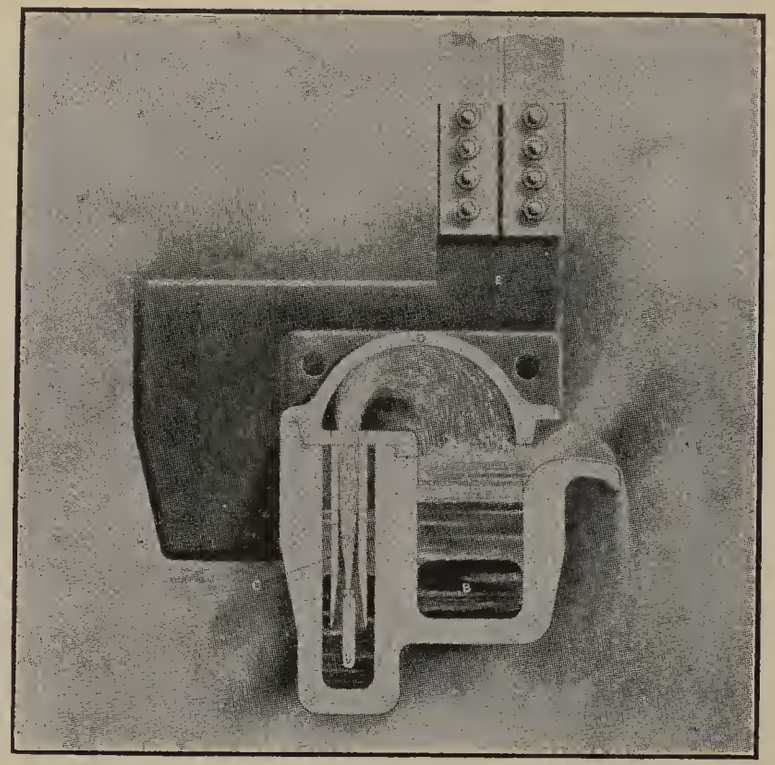

FIG. 2.

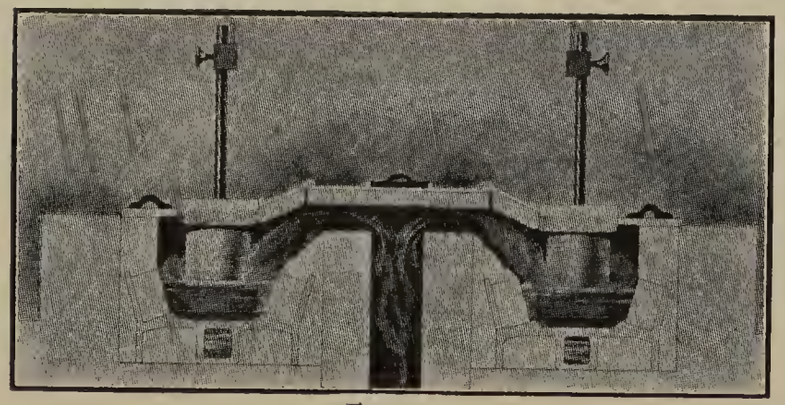

FIG. 3.

In starting a furnace, molten lead is first poured over the hearth to the requisite depth. Two of the anodes are placed in position, but these anodes are equipped for starting purposes, with a number of small carbon rods or "pins" about one inch in diameter and five inches long, which are fitted into the lower end of the anode proper and from which they extend into the lead. When these anodes are in position the salt is shoveled into the furnace until they are entirely surrounded and covered up, after which the furnace is cut in in series with all of the other furnaces. The full current passes down the starting anodes and through the small carbons or pins, which soon become red hot and later almost white hot, causing the surrounding salt to melt and the entire furnace and contents to gradually come up to the working temperature.

This method of starting one electrolytic furnace normally employing a very heavy current at low electromotive force while in series with a number of other furnaces in regular operation and using the same current, leaves nothing to be desired. There is no fluctuation whatever in starting. The rapidity with which the furnace is brought up to the desired temperature is under perfect control and is regulated by the number of carbon pins which are attached to the lower end of the regular working anodes.

The furnaces at Niagara Falls are started on 4 volts and if the furnaces are entirely cold are held at 4 volts for some time in order to bring up the temperature gradually. During all of this time the voltmeter needle remains stationary. The bath gradually becomes fluid, the lead entirely fluid and the temperature the same as the bath. When this condition is obtained the furnace is ready to operate and the carbon pins are broken off from the lower end of the anodes after which the current passes from the working face of the anodes through the salt to the lead cathode, chlorine is liberated in great volume at the anodes, and sodium deposited in the lead cathode. The steam is now turned on and caustic soda appears in the caustic chamber.

The reaction which would take place in the converter pipe if steam was injected into nothing more than red hot lead can be appreciated to a certain extent, but when the red hot lead contains metallic sodium one would naturally expect a somewhat violent reaction. As a matter of fact, however, the apparatus is

so proportioned that the circulation and decomposition proceeds smoothly to all outward appearance and is under the most perfect control. If the upper part of the cover should be cut away and the steam turned on, a scattered mass of lead would be thrown up into the air six or eight feet high, thus illustrating the positiveness of the circulation.

The caustic as it leaves the furnaces has usually a grayish or greenish color due to traces of iron and manganese, which it contains. The caustic from all the furnaces is collected and allowed to stand in settling pots for a few hours until it becomes perfectly clear and transparent, when it is packed in drums of about 735 pounds each, net weight. This caustic, as finally packed, generally tests over $99^1/_2$ per cent. soda. The method of collecting the caustic from the furnaces and conducting it to pots, which was first installed at Niagara Falls, proved unsatisfactory, but an improved system for running the caustic to the pots in a molten condition is being installed.

In determining the dimensions of the furnaces which were first installed in the works at Niagara Falls, the experience which we had previously had with 1700 ampere furnaces was our sole guide. The most suitable current density for 1700 amperes had been determined by experience, and the same current density was decided upon for the 8000 ampere furnace, five anodes being employed in each furnace. The various proportions of the new furnaces were determined in accordance therewith. When the works started it was found that the efficiency was not as high as it was in the 1700 ampere furnace, and the cause was later found to be due to low current density. As a result, the fifth anode was in time removed from all the furnaces, the furnace castings made for five anodes being gradually replaced by those made for four anodes. While this change was being brought about, the caustic end of the furnace casting was reduced to a degree of simplicity, which it seems likely, can hardly be improved.

We employ a current of 8000 amperes, which is used in one series of furnaces with four anodes to a furnace; each anode, therefore, conducts a current of 2000 amperes, which fuses the salt, maintains the temperature at a low red heat and decomposes it, the current density being 2750 amperes per square foot.

The furnaces work at seven volts between the terminals. The seat of about one-fourth of the resistance in the present instal-

lation is in the copper connected with the anodes, which was originally too small for five anodes and when the change was subsequently made to four anodes it was still worse. After unnecessary resistance is eliminated, these furnaces will work at 6 volts, average for the entire plant, when cold salt is fed into the furnaces.

There is no wear and tear on the anodes due to chemical or electrochemical causes. Indeed, there is no corrosion nor disintegration whatever in the bath. The weakest point of the anodes is the connection between the copper and the carbon, and this gradually fails because of the strain to which it is subjected, and has to be renewed. There is some breakage due to careless handling and to careless charging of salt in the furnaces, which is done with ordinary scoop shovels, but requires to be shoved down into the molten salt and between the anodes, long steel bars being used for this purpose.

The average production of each of the 45 furnaces now running, with a larger number provided for, is 581 pounds each of solid caustic soda per day and an equivalent of chlorine. The current efficiency in the process is indeed remarkable. The average of all the furnaces is now 93 per cent., and with no good reason why it should not be increased. Individual furnaces have been operated for days at a time at an efficiency so close to 100 per cent. that with the ordinary methods employed by the inspectors in the works for recording the current, weighing the caustic, etc., the efficiency is set down as 100 per cent. because it is the nearest whole number available. This high current efficiency is largely due to the immediate and effective removal of the sodium from contact with the chlorine and also from the salt except in the form of a very weak and heavy alloy. An alloy of this character is very stable and holds tenaciously to the sodium until it is carried into the converter, where the steam removes it to such an extent that there is hardly a trace of sodium left.

Whether exactly the right quantity of steam is employed or a quantity vastly in excess of that required to oxidize the sodium makes no difference whatever in the anhydrous character of the caustic, it must be readily understood that this operation proceeds at a temperature which precludes the possibility of the caustic taking up water ; as a matter of fact, the furnace tenders usually employ a slight excess of steam over that required to simply

oxidize the sodium. The hydrogen issuing from the caustic end of the furnace burns continuously in a large flame.

There is some analogy between the contact process for the manufacture of sulphuric acid and the process just described in that the one produces sulphuric anhydride and if any of the lower tests of sulphuric acid are desired the product first produced would have to be diluted with water ; in the same way it would be necessary to dilute the caustic manufactured by this process if any of the lower commercial tests were required.

I have called particular attention to the anhydrous character of this caustic by reason of a reference which some time ago appeared in a foreign electrochemical journal. The mechanical separation of the lead and caustic alkali is complete and perfect, and there is no reason why it should be otherwise.

The lining of the furnace walls is exceedingly simple. It is composed of two rows of magnesite brick placed on end around the hearth of the furnace. No mortar or cement is employed to hold the bricks in place and nothing is required. They are inclined outwardly and have no tendency to move. The salt penetrates between them in starting up a furnace, but soon freezes between the bricks in the outer row and makes the lining impervious. The present type of furnaces have never been relined.

I might reply in detail to other references which have appeared in periodicals, but the description which has been given will probably cover all points. I might say, however, that the works have been in continuous operation since current was first turned on, which was in December, 1900, the only interruption of consequence (about one week) being due to a fire at the power-house.

The Niagara Falls Hydraulic Power and Manufacturing Company delivers on our premises without loss to us a direct current of 8,000 amperes and 300 volts, or 3,250 electrical horse-power, which is and has been continuously used in connection with this process.

The same furnaces have been used satisfactorily in the manufacture of other products, notably barium hydrate and potassium hydrate, and the author believes there are other fields in which they may be usefully employed.

DISCUSSION.

Mr. C. Hering: What about chlorine? You do not say anything about chlorine. I would like to ask the author of the paper whether he attempts to collect the chlorine, and if so, how—if I am not asking any secrets—and whether he has not had considerable trouble with corrosion, due to the hot chlorine gas.

Mr. A. von Isakovics: Mr. Chairman, I intended to ask the same question and in addition, whether it has been attempted to make use of the chlorine by forming hydrochloric acid.

Mr. Henry S. Blackmore: I would like to ask in regard to the impurities in the salt employed, such as chloride of magnesium, chloride of calcium, sulphate of calcium, etc. Are they removed prior to electrolysis and, if so, how is it accomplished?

If they are not removed prior to electrolysis, do not magnesium and calcium together with the sodium formed unite with the lead, producing alloys therewith? Upon the oxidation of the sodium content of the lead alloy with steam, in the formation of sodium hydroxide, does not this also naturally oxidize the calcium and magnesium, if present, forming calcium oxide and magnesium oxide, thereby contaminating the caustic soda produced?

I would also like to ask how the chlorine is removed from the anode chamber; is it by natural displacement of generated chlorine, or mechanical suction, or blast of air? If by suction or blast of air or other inert gas does such gas present interfere with the absorption of chlorine by lime in the production of bleaching powder and what is the average percentage of such inert gas?

Mr. C. E. Acker: Whatever calcium or magnesium is contained in the salt goes into the lead. Lead takes up calcium with avidity, as it does also magnesium. It takes up all of the metals contained in the electrolyte with the exception of iron, and I think it possibly may take up a very little iron. Whatever metals have gone into the lead will be taken out by the steam. Some of them, such as calcium and magnesium are probably taken out quicker than the sodium in the form of oxide or hydrated oxide and go over with the caustic soda as an impurity. Of course the quantity present is small and does not make any particular difference in the production of caustic soda.

I might say that the caustic soda produced in these furnaces, that is to say at the time of its formation and delivery from the furnaces, is stronger than when it is finally packed. This will be expected, however, when it is understood that the caustic is thereafter more or less exposed to the air and takes up some carbonic acid therefrom. As it is finally packed the caustic usually contains about ¾ of 1 per cent. of carbonate and I think that is possibly the average. It is possible there may be some carbonic acid gas in the steam. I don't know. I never looked into that at all.

(By the use of the lantern the picture showing cross-section of two furnaces enclosed in brickwork is thrown upon the screen.)

The setting of the furnaces was at first unsatisfactory and as previously explained in the paper, they were not at first of the right size for 8000 amperes, and had five anodes. The furnaces had to be made smaller and fitted with four anodes instead of five. The illustration shows a cross-section of two furnaces. Gas is liberated at the anode and escapes from the surface of the melt and is drawn away through side passages in the brickwork by means of suction, that is to say, an artificial draft equivalent to about one-eighth of an inch is produced by means of a fan on the other side or beyond the bleach plant.

The side passages or chlorine ports have removable iron covers lined with soapstone so that the chlorine does not come in contact with iron at any point. The chlorine ports are very wide and sufficiently large to prevent choking up. At first there was considerable trouble of this sort caused by the salt gradually accumulating in the ports, but afterward the removable iron covers lined with soapstone were provided so that they could be readily opened. The cold salt is fed into the furnaces by means of ordinary scoop shovels and the furnace is always at least half-filled with this cold salt which slopes down from the front (indicating) between the anodes over toward the back of the furnace about half way. It takes some time for the cold salt to melt. It has to be brought up gradually. The men by means of bars pull back one of the front covers and shove the salt down between the anodes so that it comes in contact with the molten salt, the average depth of which is only five or six inches.

At first the men who were not experienced used to get this mass of salt worked around on the other side of the furnace. Some of

it used to get shoved up into the chlorine ports so that they were partly blocked, but that difficulty was entirely removed, as just explained.

After leaving the experimental plant in Jersey City, where we used a current of 1700 amperes, we felt sufficiently sure of ourselves to go ahead and build a large number of furnaces for 8000 amperes, and we were probably as successful at the outset as could be expected, or possibly a great deal more so.

The works at present are satisfactorily conducted and are worked at a very good profit. We have had more or less trouble and up-hill work at one time and another, almost entirely due to the low current density employed in the furnaces. Whatever irregular working there was at first was afterward found to be directly or indirectly due to low current density, for when this was largely increased and brought up to about 2700 amperes per square foot of anode surface the efficiency increased immediately to a remarkable extent and everything else fell into regular working condition.

We had considerable difficulty with the bleaching powder at first owing to a small amount of hydrochloric acid contained in the chlorine gas. A gentleman asked why we did not go into the manufacture of hydrochloric acid by combining hydrogen and chlorine. Our object had always been to make bleaching powder, and we had no desire to make any hydrochloric acid whatever; but, nevertheless, we did make hydrochloric acid in some unexplained way. This was found in the chlorine and it proved detrimental. We never investigated the source of the hydrochloric acid found in the chlorine, and I don't know exactly where it came from, but I do know that since we got the present type of furnace equipped with four anodes working at the exceedingly high current efficiency I have mentioned, that the hydrochloric acid disappeared, and we have since been successful all along the line.

A paper read at the Inaugural Meeting of the American Electrochemical Society, Philadelphia, April 4, 1902, President Richards in the Chair.

ON THE RELATIVE VELOCITIES OF THE IONS IN SOLUTIONS OF SILVER NITRATE IN PYRIDINE AND ACETONITRILE.[1]

By Herman Schlundt.

Although the velocities of the ions have been extensively investigated in aqueous solutions, the subject of ionic velocities in non-aqueous solutions has received but limited study. Determinations of transference numbers in alcoholic solutions have been made of a few salts by Hittorf, Lenz, and others, but apparently no attempts have been made to determine transference numbers in solvents other than alcohols and water. It is the object of this investigation to make a beginning in determining transference numbers with other solvents that yield solutions which conduct fairly well, and at the same time to ascertain, in a general way, the effect of dilution upon the relative velocities of the ions.

For several reasons solutions of silver nitrate in pyridine and methyl cyanide were chosen for this investigation. These solutions conduct well, and the volumetric estimation of silver by Volhard's method is rapid and accurate. Again, pyridine, as is well known, forms definite compounds with silver nitrate; *i. e.*, silver nitrate crystallizes out with pyridine of crystallization yielding the compounds $AgNO_3.2C_5H_5N$ and $AgNO_3.3C_5H_5N$. And in perusing Hittorf's classical researches on migration velocities, it was noted that the relative velocity of the cation increases with the dilution, as a rule, in solutions of such salts as show a marked affinity for water; *i. e.*, salts, which, in the anhydrous state, are strongly hygroscopic, and which, for the most part, crystallize out with water of crystallization; copper sulphate and ferric chloride are good examples. On the other hand, salts showing relatively weak affinity for water, yield transference numbers for the cation which vary but little, or decrease with the dilution; potas-

[1] For further details and data see *Journal of Physical Chemistry*, March, 1892.

sium chloride and silver nitrate will serve as examples. Now since pyridine and silver nitrate have a strong affinity for each other, and the same is true of acetonitrile and silver nitrate, we should expect the transference number of the cation in solutions of silver nitrate in pyridine to increase with increasing dilution, analogous to the behavior of solutions of salts which have a marked affinity for water. The results given in the following table show this to be the case.

TABLE I.

[Transference number of the silver ion in solutions of silver nitrate in different solvents at different dilutions. The dilution numbers indicate the number of liters of solution containing one gram-molecule of $AgNO_3$.]

	Dilution.						
Solvent.	0.5	1	2	4	10	40	100
Water	0.52	0.50	0.48	0.47	0.47	0.47	0.47
Pyridine	....	0.33	0.34	....	0.39	0.44	....
Acetonitrile	....	0.38	....	0.42	0.45	0.47	....

The transference numbers of the silver ion in aqueous solutions are taken from the work of Hittorf. My results were obtained with the form of apparatus devised by Löeb and Nernst; the experiments were conducted at room temperature.

The transference numbers were calculated from the changes in concentration about the electrodes obtained by the partial electrolysis of the solutions between silver electrodes. The electrolysis was discontinued before the so-called middle layer had changed in concentration. The silver nitrate used was fused to obtain it perfectly anhydrous and neutral. The pyridine and acetonitrile were carefully dehydrated and then distilled.

From the table it appears that there is considerable difference in the relative velocities of the ions in solutions of silver nitrate of the same concentration in different solvents. In aqueous solutions we see that the velocity of the cation decreases with increasing dilution ; while in the solutions of pyridine and acetonitrile the opposite holds true, thus showing the marked influence of the solvent upon the relative velocities of the ions.

How are these variations in the velocity of the ions with the dilution to be explained ? They *may* be explained by assuming the presence of various complex ions in the solutions ; thus, for example, A. A. Noyes,[1] in his recent investigations on transfer-

[1] *J. Am. Chem. Soc.*, Jan., 1901.

ence numbers in aqueous solutions, cites the case of barium chloride, a salt which in aqueous solutions behaves like silver nitrate dissolved in pyridine or acetonitrile, *i. e.*, the velocity of the cation increases with increasing dilution. In explanation of this change in the velocity with the dilution, Noyes states that it is necessary to assume that there is present a considerable quantity of complex negative ions formed by the union of one or more chlorine ions with one or more chloride molecules, *e. g.*, $BaCl_3'$ or $BaCl_4''$, and that these dissociate with increasing dilution. For the opposite behavior of the cation, *i.e.*, *decrease in velocity with increase of dilution*, as is the case of strong aqueous solutions of silver nitrate, we must on this basis assume the existence of complex *positive* ions in the solution, and that these dissociate with increasing dilution. For solutions of such salts as show but little or no change in the velocities of the ions with the dilution, we should have to say that but few complex ions exist ; or assuming their existence, the number of each kind, positive and negative, is about the same, and that they dissociate at about the same rate with increasing dilution. To explain the opposite behavior of the solutions of silver nitrate pointed out above, in different solvents, on this basis, it is necessary to assume the existence of complex *positive* ions in aqueous solutions, and complex *negative* ions in the pyridine and acetonitrile solutions. From these cases it is evident that the rôle of the solvent, to which the assumed existence of these various complex free ions, oppositely charged, must be ascribed, is a very important one. The important influence of the solvent, it seems to me, is generally not sufficiently emphasized in such explanations which assume that the variations in the transference numbers is due to the existence of complex free ions of the solute. Moreover, in view of the parallelism here pointed out between the affinity of the solvent and dissolved substance, and the change of the transference numbers of the ions with the dilution, it seems to me that the true explanation for these variations in the ionic velocities lies in a complex union of solvent and dissolved substance, and not in the assumption of several kinds of complex free ions of the solute.

LABORATORY OF PHYSICAL CHEMISTRY,
UNIVERSITY OF WISCONSIN,
MADISON, WISCONSIN.

A paper read at the Inaugural Meeting of the American Electrochemical Society, Philadelphia, April 5, 1902, President Richards in the Chair.

ON A NEW TYPE OF ELECTROLYTIC METER.

By Dr. Konrad Norden.

The well-known electrolytic meter is now generally considered as but little more than an antiquated device of mere historic interest. Though Edison has given his serious attention to its development, he has not been able to overcome its obvious disadvantages, nor succeeded in introducing the apparatus into practical use on any extensive scale. Other types of meters, which are based on an electro-magnetic effect, have proved superior to the electrolytic meter, and practically removed it as a competitor.

Final practical success, however, is nothing but the survival of the fittest among all competitors. It is promoted both by the further differentiation or addition of useful properties to the survivor and by the infirmity of its rivals.

The new type of electrolytic meter, which I have the honor today of describing before this association, seems to claim both of these advantages. For it is designed not merely for measuring ampere-hours, as is the case with all the other electrolytic meters, but it is also a so-called maximum meter, registering also the ampere hours during which the current rate has exceeded a certain limit. It also permits an estimate of the latter portion of the total within reasonable limits.

On the other hand, such an apparatus meets with comparatively little competition. Anything that fulfils the foregoing conditions, if based on electro-magnetic principles, is complicated as well as costly. The type of maximum meter, which is known in the art as the Wright meter, has found its way into practice only for lack of anything better, and is by no means a perfect instrument.

It appears from these considerations, that the well justified prejudice against the ordinary electrolytic meter is not applicable to the present one, which is a distinctly new apparatus. The in-

strument consists chiefly of a cell with polarizable electrodes, and its action is explained as follows:

As is well known, electrolytic decomposition in an electrolytic cell or voltameter with polarizable electrodes requires a certain well defined minimum voltage between these electrodes—the so-called decomposition electromotive force. This must be equal and opposite to the electromotive force of polarization, which latter is manifested by the appearance of the products of electrolysis at the electrodes. This point of decomposition, which must be exceeded to produce electrolysis, has a definitely marked value for a given system; therefore, the appearance of the effect of electrolytic decomposition can be considered as a sharp indicator of any voltage beyond the critical point. Moreover, a maximum current can also be indicated by this cell if it is connected in parallel with a main current resistance, which is calculated so that at the maximum current rate the drop of voltage between its ends become equal to the decomposition potential of the cell;—in other words, the ordinary shunt arrangement, such as is used with measuring instruments.

The critical point of decomposition, which depends upon the character and concentration of the electrolyte, and also, to a certain extent upon the material of the electrodes, can be varied within a wide range and brought to any desired value by simply varying the before-mentioned factors or by connecting in series several of the cells.

By means of such an apparatus, not only a maximum current is indicated, but also the ampere hours sent through the circuit above a fixed ampere rate can easily be determined, if only suitable arrangements are provided for measuring the amount of the products of electrolytic decomposition on one or both electrodes. In the case of gases, for instance, these can be collected in a calibrated glass vessel, permitting the direct reading of their volume.

Thus far the apparatus seems only to allow of the determination of the value of a product of two unknown factors, *viz.*, that of current and time, but does not give an idea of the rate of this current, except that it has been beyond a certain limit. A fair estimate, however, of the current factor itself (and consequently of the time factor) can also be secured by connecting in parallel several of these cells, which differ as to their decomposition voltage. To illustrate this scheme, we may consider an example, in

which the highest admissible current shall be perhaps equal to 300 amperes. The meter may consist of two electrodes of platinum, sponge and acidulated water as electrolyte. The critical point of decomposition for this system amounts to about 1.0 volt. If the main circuit resistance to be connected in parallel with the meter is made equal to $^1/_{300}$ of an ohm, any current higher than 300 amperes sent through the resistance will produce decomposition in the cell. We may now connect a second cell in parallel to the first one, but using a different electrolyte or electrodes of different material, we make the critical point of the cell, say, 1.33 volts. To produce this potential between the terminals of the cell, a current of 400 amperes must flow through the main shunt. No current below this value could operate the second meter, while the first meter would answer to any current over 300 amperes. The difference between the indications of the various meters, therefore, must give the ampere hours at current rates between 300 and 400 amperes. By connecting in parallel as many different cells and drawing the limits as close as desired, we can determine the current factor as definitely as may be required.

As previously stated, the property, which produces practical success of any new industrial device, is that it meets the requirement of usefulness and fulfils a real need in the art. This, I believe, can be safely said of such a meter as I have described. A large opening seems to exist for its introduction in connection with the well-known differential tariff system for electrical plants, which is practiced already on the other side of the Atlantic, and it is undoubtedly true that if any accurate meter could be had which would register not only the total current consumption, but also the variations, this system would become universal. In combination with this system, the Wright maximum meter has been used until now; but this apparatus is a mere indicator of the maximum current and does not show either the duration of this maximum current nor its absolute value. It shows merely that the current exceeded a given amount. A single accidental short-circuit, which would instantaneously blow a fuse, would cause the Wright meter to register, and the customer's bill would be in accordance with this registration. The meter which I have described gives the absolute values of the current and the length of their duration, and finally, a complete summation of the total ampere-hours supplied to the circuit, so that a single instrument

could supplant both the recording ampere-hour meter and the Wright demand meter, fulfilling the functions of both and giving more accurate records of the character of the road.

Another application is as follows: It is recognized now more and more in practice, that an exceeding rate of charging or discharging current is very harmful to storage batteries; therefore regular inspection of accumulator plants with reference to the charge or discharge rate seems to be desirable, and this can be easily done if meters of this kind are employed. It is also very easy to combine the said apparatus with a device which gives a warning, etc., as soon as the current limit has been exceeded, or acts upon any auxiliary apparatus as, for instance, a switch, in any desired manner.

Other special fields of application for the apparatus would develop themselves as soon as it came into use in the lines mentioned.

DISCUSSION.

Mr. C. J. Reed: I do not know that I understand what this meter is. The description does not seem to be full. As far as I could understand, it consists of a pair of platinum electrodes in dilute sulphuric acid, and the gases produced are measured. If that is what the meter consists of, it seems to me it would be entirely impractical, for several reasons: In the first place, the volume of the gases will not depend upon the number of coulombs that pass through, but upon the composition of the resulting gases, and upon the amount of absorption of the gases in the solution, which, for nearly a century, has been known to be a variable quantity, varying through a range of from twenty to thirty, or even forty, per cent. So far as the determination of the voltage is concerned, I understood the paper to say that one volt would cause the evolution of gases between the spongy platinum plates in sulphuric acid. That is new to me, if it means the evolution of oxygen and hydrogen simultaneously.

The voltage at which the apparatus would transmit current would depend on the composition of the electrodes, which would never be platinum, but which would always be some compound of

platinum with hydrogen and some compound of platinum with oxygen. The resulting electromotive force of decomposition would be indefinite.

THE CHAIRMAN: The author of the paper will doubtless reply to the discussion, in the transactions of the Society.

DISCUSSION COMMUNICATED AFTER ADJOURNMENT, BY K. NORDEN.

It has not been the aim of my paper, to give the description of a concrete meter, fully developed and ready for immediate practical use. My paper treats of a new *type* of electrolytic meter, outlining only the idea of such an apparatus in a general way.

This lack of information concerning the details of the meter probably suggested Mr. Reed's theoretical objections, which, however, may be easily overcome by the practical development of the instrument.

Assuming, for instance, that in the special cell referred to in my paper, only the cathode gas is collected and measured, practically no variation in the composition of the gas would occur. The influence of the absorption can be reduced to a negligible value, if a very small amount of liquid is used, and saturated with the respective gas; an incandescent lamp would keep the cells all at a constant temperature.

As to Mr. Reed's last objection, I want to say the following:

One may or may not be in favor of the so-called "Ueberspannungs-Theorie," by which the German electrochemical school tries to explain some decomposition effects. But the *constancy* of the decomposition voltage for a given system is an *experimental fact,* no matter how any one may account for it, and on this mere fact which everybody can daily produce in the laboratory, I have based my meter.

A paper read at the Inaugural Meeting of the American Electrochemical Society, Philadelphia, April 5, 1902, President Richards in the Chair.

THE REVERSIBLE COPPER OXIDE PLATE.

By Woolsey McA. Johnson.

The electrochemical combination, zinc-caustic potash-copper oxide-copper, commonly known as the Lalande element, is, all points considered, the best primary battery of the present day. It has a low internal resistance, will stand a fairly high rate of discharge without serious lowering of the electromotive force, and is quite free from local action if rightly made. Its weakest points are its low electromotive force and the tendency to absorb carbon dioxide from the air with a consequent decrease in its total output of watt-hours.

In its modern practical form, as developed by Edison and others in this country, and by the firm of Umbreit & Matthes, of Leipzig, it has a large use wherever commercial conditions are such that its reliability compensates for its higher cost.

Various attempts have been made by Waddell, Entz, Edison and others, to develop it as a commercial secondary cell. These workers have as yet met with serious difficulties both in the plating of the zinc of the discharged cell from the ionic to the metallic condition at the negative electrode, and also from certain practical difficulties at the positive electrode, the porous copper oxide plate. Accordingly, an investigation of the electrochemical properties of this plate along the lines of Dr. Dolezalek's work in the lead accumulator was suggested to me by Prof. Nernst, in December, 1899. The work extended from January, 1900, to February, 1901, and was carried on at first at the Goettingen Physical Chemical Laboratory, and later at the Jarvis Laboratory of Trinity College, Hartford. The work was of necessity given up before a complete investigation had been made, but I thought that, nevertheless, a short preliminary note telling the results already obtained would be interesting to the members of the American Electrochemical Society. Later, I expect to take the

matter up again and make a more extended investigation on the foundations I have already laid. The following is a short résumé of the experimental work and the results obtained from my experiments.

Small plates were sawed from the positive element of the "cupron element," made by the firm Umbreit & Matthes, of about the following dimensions: Height, 8 cm., width, 3.5 cm., thickness, 0.9 cm., and weight, 75 grams. Electrical connection to the plates was already made by a copper wire as per sketch (Fig. 1). These plates consist of copper gauze on which

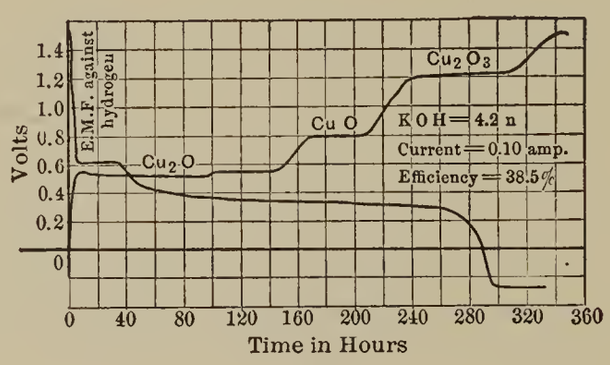

FIG. 1.

is pressed chemically pure cupric oxide made by compressing the CuOH precipitated from treating a copper sulphate solution with a caustic solution, with great mechanical pressure. Plates so formed are subsequently baked.

Two of these plates were placed as electrodes in a tightly covered glass jar filled with about 800 cc. of caustic potash solution at a distance from each other of about 5 cm. Through holes in the cover were inserted two glass tubes connecting two electrodes to serve as standards of electromotive force as per diagram (Fig. 2). The first of these auxiliary electrodes was used as the primary standard and was the so-called hydrogen electrode made as recommended by N. T. Wilsmore, in the *Zeitschrift für phys. Chemie*, V. XXV, 3, pp. 319 *et seq.* As it would be impractical to use this as a working electrode, a second electrode was inserted to serve daily as a standard. This consisted of a small glass tube connected by a siphon to the cell. In this tube was inserted a small rod of pure zinc cast with 5 per cent. mercury. The electrolyte was a solution of caustic potash of the same strength as the cell saturated with zinc by electrochemical means. The electromotive force of this electrode was fairly constant, as measured against the hydrogen electrode from week to week, and served

very well as a working standard of electromotive force in an alkaline solution. Its electromotive force against hydrogen was 0.396 to 0.415 volt, according to the concentration.

Usually a series of four of these cells were connected together in series with a bank of lamps and were placed in a thermostat.

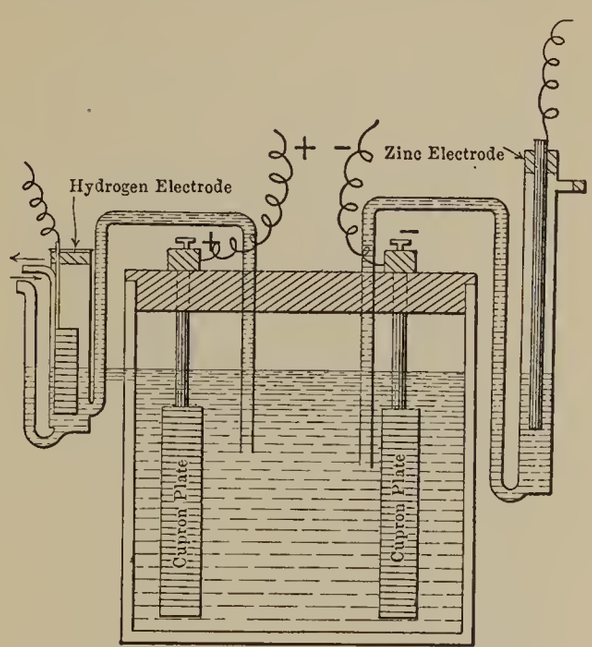

FIG. 2.

The source of current was a battery of 32 chloride accumulators of 120 ampere-hour capacity. This battery I daily charged, and as the change of voltage of the test cells was very slight and the total voltage was small in comparison with the voltage of the battery, the current was easily kept constant to a half of 1 per cent.

These plates were first completely oxidized and reduced electrolytically several times to get the active material in good working shape, and finally the action was kept up until evolution of oxygen at the anode and hydrogen at the cathode was seen with a very small current. The current was then reversed and the plates changed from oxide to copper and copper to oxide, measuring the voltage at regular intervals with a potentiometer. The readings were plotted, and we practically have the working of a porous copper plate as a reversible electrode. Curves in Fig. 1 show the reversibility and the change in the composition of the plates as affected by the electrolysis.

The efficiency as measured against the hydrogen electrode (we assume that we have an ideal reversible reservoir of hydrogen at present) is a function of the current density and the concentration of the solution. By large current densities the efficiency is

nearly a linear function of the concentration of the KOH and is extremely small for a current of one ampere. The current density cannot be expressed exactly because the real surface of the plates cannot be estimated on account of their porosity. When the current reaches 0.50 ampere the curve begins to bend some-

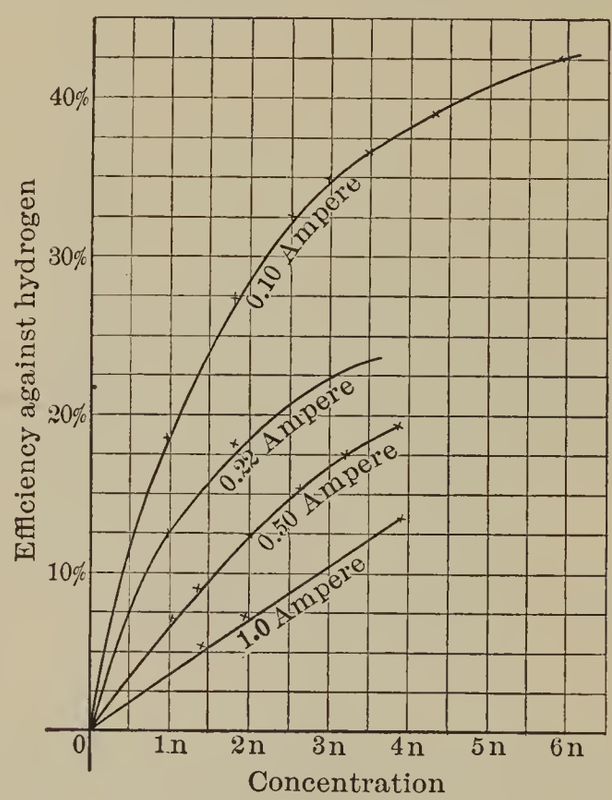

FIG. 3.

what. By 0.22 ampere this bending is much more pronounced and is very marked when the current is as low as 0.10 ampere. In fact, the efficiency is nearly directly proportional to the conductivity of the KOH solution. These bendings are not to be seen in large current densities because the scale is too small (see curves, Fig. 3).

Figure 4 shows the influence of current density on the efficiency of the plates with varying solutions. First the efficiency is nearly a linear function of the reciprocal of the current. It then increases much more rapidly and by low currents mounts steeply. The small polarization because of the concentration changes in the porous electrodes and because of changes in the electrochemical properties of the plate, and the loss of electromotive force because of the energy lost in overcoming the internal resistance of the cell, is extremely great at high current densities.

Only in the case of small current densities and concentrated solutions does the porous copper oxide plate become at all reversible. So small is the dissociation pressure of the oxide and so

great is the inner internal resistance of the plates that the reversibility cannot be compared with that of the lead peroxide plate. Here we have the peroxide of lead which is a fairly good con-

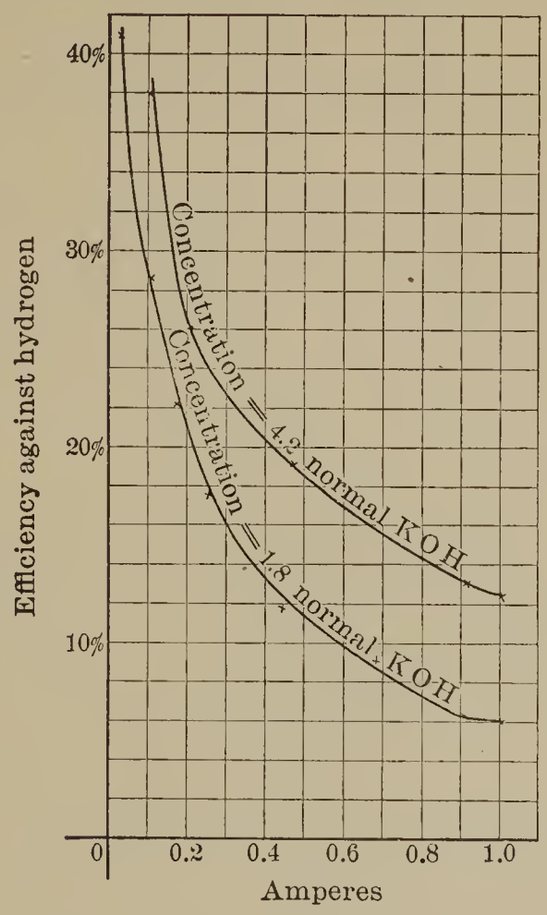

FIG. 4.

ductor of the first class, and which holds all the points of the plate at the same potential with small loss of energy. It is unfortunate that the copper oxide plate is so irreversible at anything like a working current density because the plate of 75 grams weight will give 10 watt-hours and would be an ideal plate for accumulator purposes because of its capacity and freedom from local action.

Referring to curves in Figure 1 we see that with large current densities the electromotive force increases very rapidly and in nearly a straight line. When the current is smaller the curves approach more and more the form of stairs looked at in cross-section. In Figure 1 the electromotive force mounts in the first hour to 0.50 of a volt and remains there for some fifty hours. It then mounts rapidly to 0.59 of a volt where it remains for some twenty hours. It then mounts rapidly in seven hours to 0.81 of a volt, where it remains for twenty hours. Afterward comes a second stage of slow increase for about twenty hours around 1.20 volts. It then increases suddenly to the

voltage necessary to evolve oxygen at atmospheric pressure. These stages are undoubtedly due to the electrochemical formation of various oxides of copper and can be compared to the dissociation of $CuSO_4 + 5H_2O$, remembering that instead of the pressure of the water vapor we are measuring the logarithm of the dissociation pressure of the different oxides present in the plates.

In the first stage the cuprous oxide Cu_2O is formed. The next stage is an intermediate oxide, perhaps Cu_3O_4. The third stage is undoubtedly the black CuO. The fourth stage is CuO_2, copper peroxide. No more oxides can be formed because we have now electrolytic pressure great enough to evolve atmospheric oxygen in the copper oxide plate.

On the electrolytic production of the plates we have at first, for an hour or so, a very high voltage of the superoxide of copper which at ordinary temperatures breaks up very rapidly and it changes immediately to the black oxide. Afterwards the voltage falls to about 0.37 of a volt equal to the voltage of the Cu_2O, less the loss $I \times W$. A last stage of the reduction which, strange enough, does not appear on the oxidation, belongs to the suboxide of copper. This can be seen optically by the color of the plate which it assumes in its center—an olive-green color. In fact, all these changes can be observed during the electrolysis optically as well as electrolytically.

I have measured small cells made of a Cu | CuO | KOH | H_2 | Pt combination, and found the voltage to be about 0.730 volt and to be nearly independent of the concentration of the KOH. The cell made with a cuprous oxide instead of the cupric has an electromotive force of about 0.438 volt. Further determinations of the different oxide cells will be made later.

It is my opinion as a result of this investigation that the copper oxide plate will never replace the lead accumulator no matter if a negative element of undoubted excellence were found to be combined with it to make a cell. My reasons for this are that the different oxides of copper are such poor conductors that with all current densities, which can be used in technical work, the polarization would be too great, and the fact that the copper peroxide is dissolved by concentrated KOH solutions which, of course, must be used in practical work, and that any overcharging would deteriorate the plates so fast that they never could be con-

sidered as a commercial proposition in accumulator work. In conclusion, I take great pleasure in expressing before the Society my sense of gratitude to Professor Nernst, Doctors Coehn and Dolezalek, Mr. Wilsmore, of Goettingen, and Professors Robb and Riggs, of Hartford, for their many suggestions and help in this investigation. As I have said above, the research was suggested to me by Professor Nernst and carried out on lines proposed by him.

DISCUSSION.

MR. HERING: Mr. Johnson speaks of a "slow current." I would like to ask him about what the current was, and whether it was relatively to the size of the cell, negligibly small. Also whether it was quite constant during the whole of the test.

MR. JOHNSON: I did not think the current varied over one-half per cent.

DR. H. R. CARVETH: I should like to ask if the phase corresponding to Cu_4O of the straight curve, constant voltage, is affected in the same manner as the phase in the upper one, CuO.

MR. JOHNSON: The course of the curves of change and discharge depend on the current and concentration.

DR. CARVETH: Where you have to draw lines for constant pressure, say Cu_4O, and lines for constant voltage, say Cu_2O, do you attach any importance to the curvature of the Cu_3O_4 line as to whether it is a solid solution or a compound?

MR. JOHNSON: The curves illustrate your queries.

PRESIDENT RICHARDS: I will call attention to this illustration of how electrochemistry has reacted upon chemistry in advising us of the existence of chemical compounds which, from chemical research, we had not suspected. This is only one of many cases in which different oxides and different compounds of the metals have been suspected from electrochemical work, and in some cases identified and isolated long before they were suspected or isolated chemically, so that electrochemistry has reacted upon pure chemistry, in extending, very largely, our knowledge of the number, and the properties, of chemical compounds in general. I call attention to this as one of the very fruitful functions which electrochemistry has had in its reaction upon pure chemistry.

A paper read at the Inaugural Meeting of the American Electrochemical Society, Philadelphia, April 5, 1902, President Richards in the Chair.

A THERMODYNAMICAL NOTE ON THE THEORY OF THE EDISON ACCUMULATOR.

By E. F. Roeber, Ph.D.

Contents.—§1. Accumulators of the oxygen lift type. The part which the electrolyte plays in the electrochemical action. Local concentration changes at the electrodes. §2. The volt curve during discharge. Voltage drop due to the increase of internal resistance. Voltage drop due to the change of the electromotive force proper. §3. Thermodynamical theory of concentration cells. Two different formulas for the electromotive force. §4. Application to the Edison accumulator. Calculation of the voltage drop due to the local concentration changes.

§1. The Edison accumulator aroused much discussion and interest before it was placed on the market. This is certainly due not only to the reputation of its famous inventor, but also to the evident advantages which an accumulator of the general type of the Edison cell has from a theoretical point of view. Dr. A. E. Kennelly[1] has characterized this general type by the term oxygen-lift. It is to this general type that the theory given in this paper refers.

The chemical action during the discharge of an oxygen-lift cell may be given by the equation

$$M + RO = MO + R \qquad (1)$$

where M and R are metals or metallic compounds, M being the anode and RO the cathode during discharge. During charge the reverse action takes place. In this equation, the electrolyte is omitted altogether, as it apparently does not enter into the chemical action at all; it apparently acts only as the "channel" through which the oxygen is "lifted"—to express the matter in a simple way. For the present, we will not concern ourselves with the ionic mechanism by which this lifting of oxygen is brought about.

We first want to know, what materials—what electrolyte and what electrodes—are suitable for this type of cell. It appears

[1] Transactions Am. Inst. Elec. Eng., May 21, 1901.

that any electrolyte would do which, when electrolyzed between inert electrodes, would give off hydrogen at the cathode and oxygen at the anode; but instead of using inert electrodes, we have to provide electrodes capable of oxidation and reduction and at the same time insoluble in the electrolyte. It is this last requirement—that the materials of both electrodes in all states of oxidation concerned in the electrochemical action must be insoluble in the electrolyte—which makes the practical problem so difficult and greatly limits the number of possible combinations. As materials for RO have been suggested peroxide of silver, oxides of copper, oxides of iron, and peroxide of nickel; for M, copper, cadmium, and iron, in KOH or NaOH as electrolyte. It is very doubtful whether even in this brief list all the materials mentioned meet the requirements of the problem, as sketched above.[1] For the following theory it is assumed that all these requirements are fulfilled; in other words, this theory refers to an ideal oxygen lift cell.

The question now arises: What is the ionic mechanism by which oxygen is lifted through the electrolyte? To fix the ideas, I assume that the electrolyte is an aqueous solution of KOH. The analogous calculations for NaOH can, of course, be easily made. I have already[2] sketched the ionic mechanism in a KOH solution under the ordinary assumption that the ions in this solution are the cation K and the anion OH. When $2 \times 96,540$ coulombs are given out by the cell, the reactions at the two electrodes are represented by the equations

$$M + 2\overline{OH} = MO + H_2O \qquad (2)$$

and

$$RO + 2\overset{+}{K} + H_2O = R + 2KOH, \qquad (3)$$

each chemical symbol representing a gram-molecule or gram-ion. The summation of these two formulas gives, of course, again equation (1). These two equations, however, show that the electrolyte is not merely a passive medium, but that it takes part in the electrochemical action and undergoes certain changes. One gram-molecule H_2O disappears at the R plate and appears at the M plate. 2KOH are formed at the R plate; and the 2K ions

[1] The suitability of copper is very doubtful; and the permanent insolubility of iron, when used alternately as an anode and a cathode in an alkaline solution, seems also doubtful from the results obtained by Haber and Pick (Zeitschrift für Elektrochemie, 1901, page 713).

[2] Electrical World and Engineer, **37**, p. 1105, June 29, 1091.

and the 2OH ions at the left side in the equations, represent the disappearance of 2KOH ; which proportion of these latter 2KOH disappears at the M plate and which at the R plate, can be easily calculated from the experimentally determined transport numbers of the ions in KOH, or from the relative speeds of the ions. In my former article I made this calculation and gave the numerical data upon which it is based. By taking the speed of the OH ions as three times that of the K ions, I arrived at the following result: when the cell gives out in discharge 1 ampere-second, the changes in the battery, due to the migration of the ions and to the electrochemical processes at the electrodes, consist in the transfer of 0.0000052 gram-molecule O = 0.000083 gram O from the cathode to the anode, the transfer of 0.0000026 gram-molecule KOH = 0.000146 gram KOH from the solution at the anode to the solution at the cathode, and the transfer of 0.0000052 gram-molecule H_2O = 0.000094 gram water from the solution at the cathode to the solution at the anode. The concentration of the solution at the anode therefore decreases, and that at the cathode increases ; but the *total* concentration, *i. e.*, the ratio of the total weight of KOH dissolved to the total weight of H_2O, is not changed. This result is entirely independent of the nature of the metals or compounds M and R. The numerical values, given for the local concentration changes, represent only the limits of the changes which would develop in practice, if diffusion and convection would not counteract the concentration changes. The concentration changes, really occurring in practice, will approximate the calculated values the more closely, the greater the rate of discharge of the cell, because at a very high discharge rate diffusion and convection have no time to counteract the developing concentration changes.

While I had formerly derived these results under the assumption that K and OH are the ions and that the OH ions travel with a speed three times that of the K ions, I would like to point out here that the numerical results are independent of this assumption. To calculate the concentration changes, we really do not need any conception of the ionic mechanism at all. What we need are experimental facts concerning the concentration changes which take place in a KOH solution with given electrodes, the resulting action at the electrodes being well defined. From these facts we can then calculate, what will be the concentration changes

in a KOH solution with other electrodes, if only the resulting action at the electrodes is again known with precision. In this sense the above numerical results concerning local concentration changes in an oxygen-lift cell, are merely consequences of the experimental determinations, by Wiedemann and by Kuschel, of the transport numbers of the ions in KOH. It is quite possible that in KOH solutions of such concentrations as are used in practice, the ionic mechanism will be found to be much more complicated than is expressed by the simple scheme of the traveling K and OH ions ; but this would not alter the above numerical results.

§2. The discharge curve of an oxygen lift cell shows a continuous drop of voltage, with a certain characteristic feature which will be noticed below. Let us now find to what this drop of voltage at the terminals of the cell is due.

It may, first, be due to an increase of internal resistance. An increase of internal resistance would not change the electromotive force proper, but would increase the volts lost according to Ohm's law in the cell, and would, therefore, diminish the voltage at the terminals. That there must be a variation of the internal resistance of the cell during discharge, is evident ; but it seems impossible to calculate it or even to estimate it numerically. The internal resistance of an oxygen lift cell consists of two parts : First, the resistance of the active material, from the points of oxidation or reduction to the outside terminals of the cell ; second, the resistance of the electrolyte from the parts of active material which are being oxidized at the one side to those which are being reduced at the other side. The active material of the Edison cell is made in the form of briquettes, placed in perforated nickel-plated steel boxes. The electrochemical action affects, of course, first those particles of the active material which are most easily accessible to the ions transmitting the current through the electrolyte ; *i. e.*, the particles nearest the walls of the enclosing box will first be oxidized or reduced.[1] The places of electrochemical action (*i. e.*, of oxidation and reduction) are then shifted to points lying deeper in the briquettes. At the same time the molecular structure of the briquettes changes continually, due to

[1] "The action of the charging and discharging current upon the briquettes seems to be transferred from their external surfaces inwards in a manner similar to the transfer of carbon and oxygen in the process of making malleable cast iron in the furnace on the principle of cementation." (Kennelly.)

the giving off and taking in oxygen, with a resulting contraction (at the cathode) and expansion (at the anode) of the briquettes (as stated by Dr. Kennelly). It is thus seen that the paths of the current in the active material (from the points of oxidation and reduction to the outside terminals of the cell) must continually vary and that this causes a continual change of the internal resistance of the cell. At the same time the internal resistance of the electrolyte also changes. Imagine[1] the whole electrolyte to be divided up into tubes of electric force, the walls of each tube being formed by lines of electric force and the cross-section of each tube being thus chosen that through it at any moment $1/n$ ampere flows (where n is a certain fixed large number). Then the total internal resistance may be considered to be the joint resistance of all these tubes in parallel. Now, the geometrical position and figure of these tubes will continually change during discharge, because the conditions at the ends of the tubes change, where they meet the active material: First, the particles undergoing oxidation and reduction are continually changing; secondly, the geometrical figure of the pores available to the electrolyte in the briquettes is continually changing, due to the contraction and expansion of the active material; thirdly, there are the concentration changes which develop in these pores. I think, it is thus pretty evident that it would be a hopeless task to attempt a theoretical calculation of the change of internal resistance while electrochemical action is going on. Experiments have to settle that problem.

The voltage drop during discharge may, however, also be due to a change of the electromotive force proper. When the electrochemical system which represents the cell changes, the electromotive force proper will also change. In the first place, this may be due to the fact that the total available active material of one plate has passed to another state of oxidation; then the electrochemical action which has been going on so far, must cease, and if the cell is to continue to give out current, a new electrochemical action will start. This is possible, because the materials used for the electrodes in oxygen-lift cells, can exist in quite a number of different states of oxidation. We can easily express this by equations. Instead of equation (1) we write

[1] In a way exactly analogous to the model used by Maxwell for demonstrating Faraday's views in his paper "On Faraday's Lines of Force," Trans. Cambridge Phil. Soc., Dec. 10, 1855. Scien. Pap., v. 1. p. 155.

$$M + RO_x = MO + RO_{x-1} \qquad (4)$$

where x is a whole number greater than 1. When this action must cease, because the total material RO_x has been changed into RO_{x-1}, the following action may take place:

$$M + RO_{x-1} = MO + RO_{x-2}. \qquad (5)$$

Or, if the action represented by the equation (4) ceased because the total material M had been changed into MO, the following action may take place:

$$MO + RO_x = MO_2 + RO_{x-1} \qquad (6)$$

and so on. (5) and (6) are entirely new electrochemical actions, different from (4), and different electromotive forces will correspond to these different equations. The starting of such a new electrochemical action is indicated in the discharge volt curve by a distinct bend of the curve, representing a relatively sudden change of the voltage. The general form of the discharge curve shows very distinctly the starting of the different new electrochemical actions. Attention was called to these bends in the discharge curve by Mr. C. J. Reed,[1] who had observed them in a cell of the oxygen lift type, but different from the Edison cell. The same bends in the discharge curve are also shown in some curves of the Edison battery, given in a recent lecture of Dr. S. Sheldon;[2] curves B, C, D of his figure 2, which represent the curves for the 137th, 157th, and 313th discharge of an Edison cell, show these bends very clearly, while curve A shows them to a less marked degree. The discharge curve thus shows by its form the different stages of the discharge, corresponding to different electrochemical actions. This appears to be a characteristic feature of the discharge curves of oxygen lift cells, although more experimental data in this respect would be very desirable. An intimate investigation of this phenomenon can, of course, be made only by chemical analysis.

These somewhat abrupt changes of the electrochemical system, corresponding to the starting of an entirely new reaction, are,

[1] In the discussion of Dr. Kennelly's paper Trans. Am. Inst. Elec. Eng., May 21, 1901.

[2] Electrical World and Engineer, 1902, February 22, page 346. (I am not quite sure that the above explanation of the bends tells the whole story in the case of Dr. Sheldon's voltage curves of the Edison cell. It is suspicious that the curve for the first discharge is quite smooth and does not show nearly as many sharp bends as his curves for the later discharges. This would apparently indicate that the cell is in a different condition after numerous discharges from its initial condition. Have ferrates or ferrous hydrate been formed in the series of discharges and charges? In that case the Edison cell would not be an oxygen-lift cell.)

however, not the only changes which the system undergoes during discharge. There is also a continuous change of the system due to the local concentration changes in the pores of the two plates. This continuous change of the system, due to concentration changes, is necessarily accompanied by a change of the electromotive force proper, and, as will be shown presently, it is possible to investigate this problem theoretically by very exact and well established thermodynamical methods.

The question is this: Assume two oxygen-lift cells of the same type, but differing in so far as in the one, concentration changes, developing during discharge, cannot easily be destroyed by diffusion or convection, while in the second cell they can, or, still better, assume this second cell to be so large, with so large pores and so much solution in these pores that when the same number of coulombs is taken out of each of these cells, perceptible concentration changes develop in the first cell, while those developing in the second cell are so small that they can be neglected.[1] To distinguish both cells, I will, for the sake of brevity, call the first the "small" cell and the second the "large" cell. Assume that both cells are filled with a solution of the same concentration; they have been charged and have been allowed to stay at rest on open circuit for a time long enough that all concentration differences developed during charging have disappeared, so that in both cells the concentration of the electrolyte is uniform throughout. Both cells will then have the same electromotive force (measured at open circuit), as all parts of the electrochemical system are under exactly identical conditions in both cells.

We then connect both cells in series and begin to discharge them. After a certain number of coulombs have been given out, we open the circuit and ask: What has been changed in the cells?

[1] When, for instance, 96,540 coulombs are taken out of each cell, in either cell 14 grams KOH disappear in the pores of the anode and appear in the pores of the cathode, and 9 grams H_2O disappear in the pores of the cathode and appear in the pores of the anode (see § 1). Let the solution originally be about 20 per cent. KOH, so that 1 cc. contains 0.24 gram KOH and 0.94 gram H_2O. Let the volume of the solution in the pores of each plate of the first or smaller cell be 100 cc., and that of the second or large cell be 2,000 cc. Then in the beginning the solution in the pores of the anode of the first cell contains 24 grams KOH and 94 grams H_2O; after 96,540 coulombs have been taken out, it contains 10 grams KOH and 103 grams H_2O, so that the concentration has decreased from about 20 per cent. to 9 per cent., which is a considerable change. On the other hand, the solution in the pores of the anode of the second cell contained originally 480 grams KOH and 1,880 grams H_2O, and after 96,540 coulombs have been taken out, it contains 466 grams KOH and 1,889 grams H_2O, so that the concentration has decreased from slightly above 20 per cent. to slightly below 20 per cent., which is insignificant. This numerical example is given only as a rough illustration of what is meant by the above schem

The same number of coulombs have flown through both cells in the same direction. In either cell the same number of grams of oxygen have been transported from the nickel cathode to the iron anode; in this respect, therefore, both cells are still exactly alike. But while in the large cell no concentration changes have developed, in the small cell the concentration has decreased in the pores of the iron anode and has increased in the pores of the nickel cathode. The total concentration of the electrolyte (which will be defined as the ratio of the total number of gram-molecules of KOH dissolved to the number of gram-molecules of H_2O) is still the same in both cells; but while the concentration has remained uniform in the large cell, it is no longer uniform in the small cell. Hence the electrochemical system represented by the large cell is no longer identical with that represented by the small cell, the only difference, however, is that in the former the concentration is uniform, in the latter it is not. To this difference in the constitution of these two electrochemical systems will correspond a difference of the electromotive forces of both systems; both cells will no longer have exactly the identical electromotive forces. For our present purpose we are not interested in the value of the electromotive force of each cell; we are only interested in the difference of the electromotive forces of both cells, because this difference represents exactly what we are after, namely the change of electromotive force, due to the local concentration changes alone.

Now, this difference of the electromotive forces of both cells is

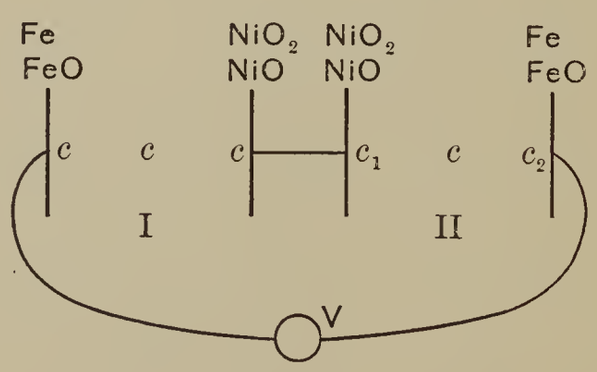

FIG. 1.

measured by connecting both cells in series, but one against the other, as shown in Fig. 1. There are two Edison cells, I and II; the concentration c is uniform throughout the cell I, while in II the concentration c_2 in the pores of the iron plate is smaller than c and the concentration c_1 in the pores of the nickel plate is

correspondingly larger. The nickel plates of both cells are directly connected by a wire and the iron plates are connected together through a high resistance voltmeter, or capillary electrometer, or quadrant electrometer, etc. This instrument, V, then measures the difference of the two electromotive forces of the cells.

Where does this difference come from? For this purpose let us consider the two cells, connected together as shown in Fig. 1, as one total electrochemical system. The electromotive force of this new combined system (which is the same as the difference of the electromotive forces of the two single cells) can be calculated by allowing this total system to give out current, say for charging the quadrants of the quadrant electrometer V. Then the same number of coulombs flow through both cells; let us assume that the current flows in the direction indicated by the arrow in the figure,[1] *i. e.*, from the iron to the nickel plate in cell I and from the nickel to the iron plate in cell II; in other words, cell I is discharged, while cell II is charged. The same amount of oxygen which is transferred from the nickel plate to the iron plate in cell I, is transferred from the iron plate to the nickel plate in cell II, so that the same amount of Fe which is changed into FeO in cell I, is changed from FeO into Fe in cell II, and the same amount of NiO_2 which is reduced to NiO in cell I, is formed back from NiO in cell II. Hence the total amount of Fe in the total system is not changed in the least, while the system gives out current; nor is the total amount of FeO in the total system changed, nor that of NiO_2, nor that of NiO. The only change in the system, taken as a whole, is a change of local concentrations in cell II. Cell I is so large that no concentration changes can develop, according to our assumption. But in cell II the current, when flowing in the direction assumed, changes the concentrations c_1 and c_2 in the pores of the two plates, and, as can be easily seen,[2] in such a way that c_1 decreases and c_2 increases; in other

[1] This assumption leads to correct results in the thermodynamical calculations given in §4, while the assumption of the opposite direction of the current would lead to contradictions. The calculations in §4 are therefore the proof of the correctness of the above assumption. This assumption can also be considered as a consequence of the general rule that when a concentration cell gives out current, it flows in such a direction that the existing concentration differences are equalized. This rule follows directly from the second principle of thermodynamics.

[2] Cell II is charged, the nickel plate is anode, the iron plate cathode. The concentration decreases in the pores of the anode and increases in the pores of the cathode. In our case c_1 is larger than c, but decreases when the system gives out current; on the other hand c_2 is smaller than c, but increases when the system gives out current.

words, the existing concentration differences in cell II are equalized, while the total system gives out current, and this is the only change which takes place in the total system. The total system of Figure 1 represents, therefore, a so-called concentration cell. The electromotive force of a concentration cell, however, can be exactly calculated by thermodynamical methods, as has first been shown by Helmholtz. In § 3 I will give a review as concise as possible, of the thermodynamical theory of concentration cells. Although the formulas and results arrived at in §3 are, of course, not new, I believe the way by which I develop them is rather simple and somewhat novel (not in principle, but perhaps in form); and for this reason I hope this brief review may be welcome to some who are interested in this subject. The application of the theory to our problem of the Edison cell will be made in § 4.

§3. As a concentration cell, in its most general sense, I define a galvanic system capable of giving out electrical energy, while the only change in the system is a change of concentrations. For instance, when in a cell

$$Zn,\ ZnSO_4\ (c_1),\ ZnSO_4(c_2),\ Zn$$

(c_1 and c_2 representing two different concentrations of $ZnSO_4$ in aqueous solution) the current flows in the cell from c_1 to c_2, the same amount of Zn dissolves in the c_1 solution, as is deposited from the c_2 solution, so that there is no total change in the Zn, and the only change in the cell is a change of the concentrations of the two solutions.

Another example is a combination of two Helmholtz "calomel cells":

$$Zn,\ ZnCl_2(c_1),\ Hg_2Cl_2,\ Hg\ —\ Hg,\ Hg_2Cl_2,\ ZnCl_2(c_2),\ Zn,$$

i. e., two cells with a Zn electrode, a calomel mercury electrode, and chloride of zinc as electrolyte, are connected against one another; the concentrations c_1 and c_2 are different; when the combination of these two cells gives out current (which may flow in the above combination from the left hand to the right hand), then the amount of Zn dissolved in the left cell is deposited in the right cell, and the same amount of Hg_2Cl_2 which is reduced to Hg in the left cell is formed from Hg in the right cell, hence there is no change in the total amounts of Zn or Hg_2Cl_2 or Hg; the only change in the whole combination is that in the left cell new $ZnCl_2$ is formed and the concentration c_1 increases, while in the right cell the same amount of $ZnCl_2$ disappears and the con-

centration c_2 decreases. The combination of these two cells together, therefore, represents a system in which, when it gives out electrical energy, nothing is changed but the concentrations of the electrolytes. The combination of these two cells together therefore represents a concentration cell—in the same way as the combination of the large Edison cell and the small one (at the end of §2) also represents a concentration cell. Neither a single calomel cell, nor a single Edison cell is a concentration cell ; but the combination of two calomel cells, or the combination of two Edison cells may, under certain conditions, as I have shown, represent a concentration cell. This shows how the theory of concentration cells can be applied also to the study of special problems of other galvanic cells.

The methods of thermodynamics have been applied to the theory of concentration cells in two different ways, both of which lead to useful formulas. These two different ways differ from another in the form of the cyclic process which the cell is assumed to undergo and upon which the two principles of thermodynamics are applied. In both cycles which will be described, the concentration cell is first discharged in a reversible way,[1] and is brought back afterwards to its initial condition in a different, but also reversible way. The two methods to be described differ in the way in which the system is brought back to its initial condition.

First Method.—The general idea of the first cycle to be described, is to let the cell give out a certain amount of coulombs in discharge at a fixed temperature, to change then the temperature and recharge the cell at the new temperature and to bring the cell finally back to the original temperature. The cell has then undergone a complete cycle ; as the discharging and charging has been done at different temperatures, the electromotive force of discharge is different from the electromotive force of charge ; hence, although the same number of coulombs which have been given out by the cell during discharge, have been sent back into the cell during charge, yet the electrical work performed by the cell during discharge (the product of coulombs and electromotive force) is different from the electrical work done upon the cell during charge. We, therefore, can design such a cycle that a positive amount of work has been done by the cell during the

[1] For this purpose it is only necessary to discharge the cell in such a way that the Joulean heat developed in the cell is negligible against the other quantities of energy, and that there is no diffusion (Helmholtz).

whole cycle, and we can then apply the principles of thermodynamics in exactly the same way as we do in the thermodynamics of a gas engine changing heat into work. Indeed, our cycle can be made the exact analogy to the well-known Carnot-Clausius cycle for gases.

Let the abscissas in Fig. 2 represent the coulombs given out by the cell, while the ordinates represent the electromotive force in volts. The beginning of the cycle is represented by point 1; the electromotive force at that moment may be E volts, the absolute temperature T. Let the cell give out C coulombs, and let

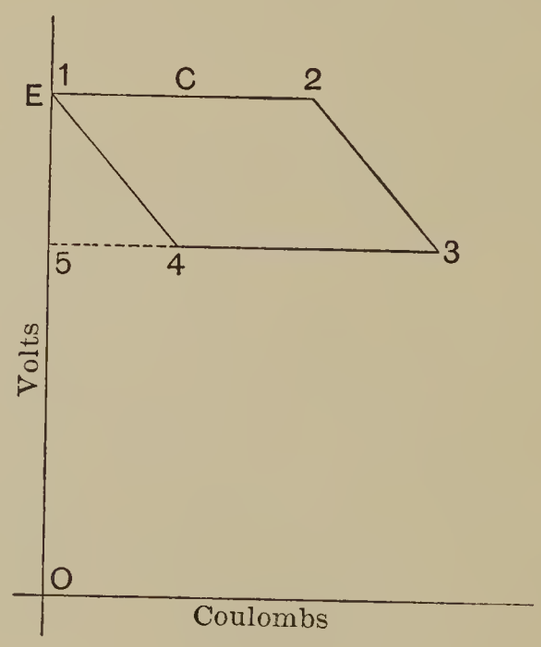

FIG. 2.

this be an infinitely small quantity, represented by line 12, by an isothermic process, *i. e.*, the temperature T is kept constant. Experience has shown that to keep the temperature constant, it is necessary either to supply heat to the cell from the outside or to give off heat from the cell to the outside. To fix the ideas, I will assume that it is necessary to supply heat from the outside; the other case can, of course, be treated in an analogous way. The amount of heat which must be supplied to the cell from the outside while it gives out C coulombs at the constant temperature T, may be Q_1 gram-calories. The heat equivalent to the total chemical change in the cell per (univalent) gram-equivalent of the material reduced at the cathode or of the material oxidized at the anode, may be h gram-calories; this corresponds to 96,540 coulombs; hence the heat which is equivalent to the chemical change due to the passing of C coulombs, is

$\frac{Ch}{96,540}$ gram-calories. The electrical work performed is EC volt-coulombs or 0.24 EC gram-calories. Then, according to the principle of the conservation of energy, we have

$$Q_1 = 0.24\ EC - \frac{Ch}{96,540}. \qquad (7)$$

The second step of the cycle is represented by line 2–3 and is adiabatic, the cell being further discharged in such a way that heat is neither supplied to the cell from the outside nor given off from the cell to the outside; the temperature of the cell will then change from T to $T - dT$; at the same time the electromotive force, which is a function of the temperature, will change from E to $E - \frac{dE}{dT} dT$. Step 3–4 is again isothermic (like 1–2), but this time the cell is charged, and to keep the temperature $T - dT$ constant, the heat Q_2 is given off from the cell to the outside. Step 4–1 is again adiabatic.

When the cycle is completed, the internal energy of the system is again the same as at the start. But the cell has performed work, because while it was discharged during the part 1–2–3 in Fig. 2, its (average) electromotive force was higher than when it was recharged on the part 3–4–1; this is at once evident from the figure. The work done during the whole cycle, in volt-coulombs, is given by the area 1–2–3–4. This area is the product of length 1–2 into length 1–5, and as 1–2 = C (in coulombs) and $1\text{–}5 = \frac{dE}{dT} dT$ (in volts), this area is in volt-coulombs

$$C \frac{dE}{dT} dT$$

or in gram-calories

$$0.24\ C \frac{dE}{dT} dT.$$

This work done by the cell during the cycle, has been done at the expense of heat of the surrounding medium. We have seen that during the step 1–2 the cell has received the heat Q_1 from the outside at the temperature T. During the step 3–4 the cell has given off the heat Q_2 to the outside at the temperature $T - dT$. The difference of these two amounts of heat has been changed into work. From the second principle of thermodynamics, as formulated by Clausius, we know that the ratio of the heat

changed into work to the heat Q_1 supplied to the cell at the temperature T, is $\frac{dT}{T}$; in other words the heat changed into work during the cycle, is in gram-calories $Q_1 \frac{dT}{T}$; hence we have the equation

$$Q_1 \frac{dT}{T} = 0.24\, C \frac{dE}{dT} dT.$$

By introducing into this equation the value of Q_1 from (7), we get

$$E = 0.000043\, h + T \frac{dE}{dT}. \qquad (8)$$

This is the well-known formula, sometimes called the Gibbs-Helmholtz modification of Thomson's rule.[1] It is valid for any galvanic cell. To apply it to a concentration cell, we have to consider that h represents the heat which is equivalent to the total change of chemical energy in the cell per (univalent) gram-equivalent of the material reduced at the cathode or of the material oxidized at the anode. For a concentration cell, consisting of two Edison cells, the "large" one and the "small" one, connected against another, as described at the end of § 2, h represents the heat which is equivalent to the total change of internal energy when in the large cell 1 gram-equivalent $= \frac{1}{2}$ gram-molecule O is transported from the nickel plate to the iron plate and in the small cell in the opposite direction. We know that the total change in the whole system is a change of concentrations in the small cell: that a certain amount of KOH is transported from one concentration of the solution to another concentration, and at the same time also a certain amount of H_2O from one concentration of the solution to another concentration. In general, we may say that the total process in any concentration cell, while 96,540 coulombs are flowing through it, consists in the transport of x gram-molecules of the dissolved substance from a concentration c_1 of the solution to a concentration c_2, and in the transportation of y gram-molecules of the solvent from a concentration c_3 of

[1] Where this formula was first given, I do not know. Helmholtz (in the introduction to his first paper, "Die Thermodynamik Chemischer Vorgaenge," Sitz. Ber. d. Berl. Ak., 1882, Feb. 2; reprinted in the second volume of his Wissenschaftliche Abhandlungen, 1883) proves that the mechanical equivalent of that heat which must be supplied to a galvanic cell during the flow of C coulombs, in order to keep the temperature constant, is $T \frac{dE}{dT} C$. This leads, of course, at once to the above formula. I am well aware that Helmholtz' derivation of this result is much more elegant mathematically than the above proof; but the above proof seems to me to be more self-explanatory.

the solution to a concentration c_4, or in a number of such transportations. x and y are fixed numerical values for a given concentration cell. The concentrations c_1, c_2, c_3, c_4 may contain a_1, a_2, a_3, a_4 gram-molecules of the dissolved substance to b_1, b_2, b_3, b_4 gram-molecules of the solvent respectively.

The heat h corresponding to this change can be easily calculated when an empirical formula is known, giving the heat corresponding to the dissolving of a gram-molecules of the dissolved substance in b gram-molecules of the solvent, as function of a and b. This heat may be represented by $f(a, b)$. Then we get, if the concentrations c_1, c_2, c_3, c_4 are not appreciably changed by the transportation of the x and y gram-molecules,

$$h = x\left[\frac{\partial f(a_2 b_2)}{\partial a} - \frac{\partial f(a_1 b_1)}{\partial a}\right] + y\left[\frac{\partial f(a_4, b_4)}{\partial b} - \frac{\partial f(a_3, b_3)}{\partial b}\right]. \quad (9)$$

This equation, in combination with (8), has been applied by Dr. F. Dolezalek[1] with remarkable success to the lead accumulator, for which all the necessary experimental data were available. The latter is, unfortunately, not the case for the Edison accumulator. For this reason I will not discuss this method any further, but will only add that Professor H. S. Carhart[2] has given an interesting modification or generalization of equation (8). His equation (which, like (8), is valid for any galvanic cell) may be derived by the cycle given above, if the cathode part and the anode part of the cell are considered separately, and the amounts of heat which are supplied during the different steps of the cycle to each of the two parts of the cell, are distinguished from another; the result is that instead of the one differential quotient $\frac{dE}{dT}$ in (8) a sum of two such differential quotients appears, referring to the two parts of the cell. It is evident that the application of Professor Carhart's formula requires the knowledge of still more empirical data; but when they are known, his formula yields a deeper insight into the processes in the cell than equation (8) does.

Second Method.—The first step of the cycle used in this method is exactly the same as that in the first method,—the concentration cell gives out C coulombs at the constant temperature T. But, while in the first method it was brought back to its initial condition in a somewhat roundabout way in which the temperature

[1] Dolezalek: "Die Theorie des Bleiaccumulators" (1901), p. 30.
[2] Carhart: Physical Review, Vol. II, 1900, p. 1.

varied, in our second method, we bring it back to its initial condition by a more direct way, in which we hold the temperature throughout constant = T. While the cycle, described in the first method, can be applied to any galvanic cell and, therefore, yields a very general result, valid for any cell, the cycle to be described now, holds good only for concentration cells. On the other hand, as we hold the temperature throughout constant during the following cycle, the second principle of thermodynamics leads to a very simple form; if we write it, according to Clausius,

$$\int \frac{dQ}{T} = 0,$$

where dQ is the infinitely small (positive or negative) heat supplied from the outside to the system at each infinitely small step of the reversible cycle and T the corresponding temperature, then as T is constant throughout, we have

$$\int dQ = 0;$$

i. e., the sum of all the (positive and negative) amounts of heat supplied to the system from the outside during the total cycle, is zero. The total work performed during a reversible isothermic cycle must, therefore, also be zero.[1] The concentration cell, while giving out C coulombs at the voltage E at constant temperature, performs the work EC in volt-coulombs or 0.24 EC in gram-calories. Hence, if we bring the concentration cell back to its initial condition by an isothermic reversible process, we have to perform the same amount of work upon the cell from the outside.[2] We accomplish this by Helmholtz's method of isothermic distillation.[3]

To fix the ideas, let us consider the concentration cell, described at the end of § 2 and consisting of the "large" and the "small" Edison cell, connected against another. The original

[1] According to the principle of the conservation of energy, in any case $Q = dU + W$, where Q is the heat supplied to a system, dU the increase of internal energy of the system, W the work performed by the system. For a complete cycle, dU is zero, because the system has come back to its initial condition; this is just the reason why the performing of a cycle, first used by Carnot, is of such a general usefulness in thermodynamical calculations. For a reversible isothermic cycle Q is also zero, which was proved above. Hence, as Q and dU are both zero, W must also be zero.

[2] Then the total work, performed during the cycle, is zero.

[3] Helmholtz: Monatsber. Berl. Ak., 1877, Nov. 26th; and his second paper "Zur Thermodynamik chemischer Vorgaenge," Sitzungsber. Berl. Ak., 1882, July 27th. These two papers are reprinted in the first and second volume, respectively, of his Wissenschaftliche Abhandlungen (1882–1883). See, also, Dolezalek: "Die Theorie des Bleiaccumulators" (1901), p. 31.

condition (at the beginning of the cycle) is that the concentration in the large cell I is uniform $= c$, while in the small cell II we have concentration differences, $c_1 > c > c_2$, in Fig. 1. The first step of the cycle is the discharge of the system, C coulombs being given out; the only change in the total system is a change of local concentrations in cell II; there disappear 0.0000026 C gram-molecules KOH at the anode (concentration c_1) and reappear at the cathode (concentration c_2), and there disappear 0.0000052 C gram-molecules H_2O at the cathode (concentration c_2) and reappear at the anode (concentration c_1). The second step of our cycle must therefore consist in transporting back by isothermic distillation

0.0000026 C gram-molecule KOH from c_2 to c_1

and

0.0000052 C gram-molecule H_2O from c_1 to c_2.

The work performed in transporting dx gram-molecule of water from a KOH solution of the concentration c_1, to a solution of the concentration c_2 by isothermic distillation, can be calculated as follows: The vapor-pressure over the concentration c_1 at the temperature T may be p_1; that over c_2 may be p_2; p_1 and p_2 are distinct fixed values, as c_1, c_2, and T are given. Assume the solution of the concentration c_1 with its vapor contained in a cylinder with movable piston. The piston is moved upwards so that dx gram-molecule of water is vaporized; the temperature T is kept constant by means of applying heat from the outside to the system; the work performed is[1]

$$p_1 V_1 dx,$$

where V_1 is the volume of 1 gram-molecule of aqueous vapor at the pressure p_1. We then take away the dx gram-molecule of steam from the solution, and treat it separately in another cylinder with piston; we bring it by an isothermic process from the pressure p_1 to the pressure p_2. It will then have the volume $V_2\, dx$. The work performed is

$$dx \int_1^2 p dv = dx \int_1^2 \frac{RT}{v} dv = dx\, RT \log \frac{V_2}{V_1} = RT \log \frac{p_1}{p_2} dx.$$

We now bring the steam in contact with the solution of the concentration c_2 (which has the vapor-pressure p_2) and treat both together again in a cylinder with movable piston, the temperature

[1] If the change of the volume of the solution (which is very small compared with the volume of the steam) is neglected.

being always held constant; we lower the piston so that the steam dx is condensed; the work performed is

$$-p_2 V_2 dx.$$

We thus have brought, by means of isothermic distillation, dx gram-molecule H_2O from the solution with the concentration c_1 to the solution with the concentration c_2, and for this purpose the system has performed the work

$$\left(p_1 V_1 + RT \log \frac{p_1}{p_2} - p_2 V_2\right) dx,$$

but as the whole process was isothermic, we have $p_1 V_1 = p_2 V_2$, and the work performed by our system is

$$RT \log \frac{p_1}{p_2} dx. \qquad (10)$$

In this calculation it was assumed that the amount dx is so small that the changes in c_1 and c_2 during the process are negligible.

The work performed in transporting one gram-molecule of KOH from a solution of the concentration c_2 to a solution of the concentration c_1 by isothermic distillation, is calculated as follows:[1] We have in one vessel the solution with the concentration c_2; it contains a_2 gram-molecules KOH and b_2 gram-molecules H_2O. In a second vessel we have the solution with the concentration c_1; it contains a_1 gram-molecules KOH and b_1 gram-molecules H_2O. In a third vessel we have an amount of pure H_2O; this is only auxiliary, and the amount of H_2O in this third vessel will be found to be unchanged at the end of the process, although it is used in the intermediate steps. The purpose of the process is to have finally $a_2 - 1$ gram-molecule KOH and b_2 H_2O in the first vessel and $a_1 + 1$ gram-molecule KOH and b_1 H_2O in the second vessel. We accomplish this by isothermic distillation as follows. For abbreviation I will write $g_1 = \frac{b_1}{a_1}$ and $g_2 = \frac{b_2}{a_2}$.

First distil g_2 gram-molecules H_2O from the third vessel (pure water) to the first vessel (c_2); the corresponding work is

$$g_2 RT \log \frac{P}{p_2},$$

[1] The following deduction differs from that given by Dr. Dolezalek on pages 31 and 32 of his book, quoted before. His deduction is certainly brief and is mathematically correct, but appears to me to be open to the objection that his term p for the varying aqueous vapor-pressure over the gram-molecule H_2SO_4 (originally pure) has no exact physical meaning.

where P and p_2 are the pressure over the pure water and over the concentration c_2 respectively. We have then in the first vessel a_2 KOH and $b_2 + g_2$ H_2O. We divide this solution into two parts: the one containing $a_2 - 1$ KOH and b_2 H_2O, the other containing 1 KOH and g_2 H_2O. No work is done in this separation, if a_2 is large against 1, because in this case the two parts have the same concentration as the solution before, so that it is simply a mechanical separation. The part containing $a_2 - 1$ KOH and b_2 H_2O is left in the first vessel, as this is exactly what we want to have in this vessel at the end of the process.

The other part which contains 1 KOH and g_2 H_2O is treated separately. It is separated into two parts: the one containing 1 KOH and g_1 H_2O, the other containing $(g_2 - g_1)$ H_2O. This is done by isothermic distillation. The work is equal, and opposite in sign, to the work done in distilling $(g_2 - g_1)$ H_2O from pure water to a solution containing originally 1 KOH and g_1 H_2O, and finally 1 KOH and g_2 H_2O. The work is therefore

$$- \mathrm{RT} \int_{x=g_1}^{x=g_2} \log \frac{\mathrm{P}}{p}\, dg = \mathrm{RT} \left[- (g_2 - g_1) \log \mathrm{P} + \int_{g_1}^{g_2} \log p\, dg \right],$$

where p is the varying vapor pressure over the KOH solution.

The $g_2 - g_1$ gram-molecules H_2O are added to the third vessel (pure water), from which before g_2 had been taken out, so that now only g_1 are missing in it.

The solution containing 1 KOH and g_1 H_2O is mixed with the solution in the second vessel, containing a_1 KOH and b_1 H_2O. No work is done in this mixture. We thus obtain $a_1 + 1$ KOH and $g_1 + b_1$ H_2O.

From this solution we distil g_1 H_2O over to the third vessel (pure water), so that this now has the same amount of water, as in the beginning, while the second vessel now contains $a_1 + 1$ KOH and b_1 H_2O; that is what we wanted. The work performed in this last distillation is

$$g_1 \mathrm{RT} \log \frac{p_1}{\mathrm{P}}.$$

When we now take all the parts of this process together, we see that the work performed in transporting one gram-molecule of KOH from a solution of the concentration c_2 to a solution of the concentration c_1 is

$$RT\left[g_2 \log \frac{P}{p_2} - (g_2 - g_1)\log P + \int_{g_1}^{g_2} \log p \, dg + g_1 \log \frac{p_1}{P}\right] =$$

$$RT\left[g_1 \log p_1 - g_2 \log p_2 + \int_{g_1}^{g_2} \log p \; dg\right]. \quad (11)$$

To sum up, our isothermic reversible cycle consists of two steps: in the first the cell gives out C coulombs in discharge and performs the electrical work

$$0.24\, E\, C \quad (12)$$

(if measured in gram-calories); in the second step the system is brought back to its initial condition by means of isothermic distillation; the work performed during this step can be calculated by means of equations (10) and (11). The work performed by the cell during the first step must equal the work performed upon the system during the second step. This gives an equation from which the electromotive force E can be calculated.

This method has been applied with good success in several cases; notably by Helmholtz, to whom it is due, to the theory of calomel cells, and more recently by Dr. F. Dolezalek to the theory of the lead accumulator. In the next section it will be applied to the Edison accumulator.

It will be seen that the two methods described above for calculating the electromotive force of a concentration cell are merely based upon the two principles of thermodynamics; *i. e.*, upon the two best established and safest principles of natural science. There is no assumption of a hypothetical nature used in the above methods.

It is well known that a very complete theory[1] of concentration cells has more recently been developed by Professor W. Nernst on the basis of the modern theory of solutions and more especially of the so-called electrolytic dissociation theory. As far as this theory can be compared with the older purely thermodynamical methods, described above, there is a general agreement between the results of both theories. But the theory of Nernst goes further than the purely thermodynamical methods. This is because Professor Nernst makes use of very distinct assumptions concerning the constitution of a dilute solution and concerning the ionic mechanism of the process at a reversible electrode; he thus ob-

[1] Nernst: Ztschr. phys. Chem., **2**, 613, 1888; **4**, 129, 1889; Planck: Wied Ann., **39**, 161, 1890; **40**, 561, 1890.

tains a very complete insight into the ionic mechanism in a concentration cell. This incontestable advantage of Nernst's theory is, however, inherently combined with the disadvantage that the basis of his theory is hypothetical.

§4. I will first briefly discuss the problem of the dependency of the electromotive force of the Edison accumulator upon the concentration of the KOH solution. For this purpose connect two Edison cells in series, but the one against the other (*i. e.*, nickel connected with nickel); the solution of the one cell has the concentration c_1, that of the other c_2. In each cell the concentration of the solution is uniform throughout all parts of the cell. If a current flows through the combination of these two cells, then it is at once evident that in the total combination the amount of NiO_2 is not changed, nor that of Ni, nor that of Fe, nor that of FeO; moreover, if we neglect at present the local concentration changes developing in the pores of the plates, the concentrations c_1 and c_2 are also unchanged; hence nothing is changed at all in the total combination; therefore the electromotive force of the electrochemical system, consisting of the two cells connected against another, must be zero; in other words, the cell with the concentration c_1 must have the same electromotive force as the cell with the concentration c_2, or the electromotive force of the Edison accumulator is independent of the concentration. A similar problem has been treated by Mr. W. McA. Johnson,[1] namely, the question how much the electromotive force of a copper oxide plate against a "hydrogen electrode" in a KOH solution depends upon the concentration of this solution. But these problems are distinctly different from the problem with which I am concerned in this paper, namely, the question how the electromotive force of an Edison cell varies with the local concentration changes developing in the pores of both plates.

For the discussion of this problem, I assume two cells connected against another, both of which have the same "total concentration," but in the one the concentration is uniform, in the other it is not; *i. e.*, we have the arrangement represented in Fig. 1. As I have already discussed this problem to some extent in the previous sections, I may now restrict myself to the exact mathematical calculation.

In the beginning of the cycle the concentration in the "large" cell

[1] Electrical World and Engineer, **39**, 90, Jan. 11, 1902.

I is throughout uniform and equal to c (a gram-molecule KOH and b gram-molecule H_2O, $g = \frac{b}{a}$); in the "small" cell II the concentration in the middle part is also c, while in the pores of the nickel plate it is c_1 (a_1 gram-molecule KOH and b_1 gram-molecule H_2O, $g_1 = \frac{b_1}{a_1}$); in the pores of the iron plate it is c_2 (a_2 gram-molecule KOH and b_2 gram-molecule H_2O, $g_2 = \frac{b_2}{a_2}$); c_1 is larger and c_2 is smaller than c.

The first step of the isothermic cycle is that the system, consisting of the two cells, gives out C coulombs; it performs the work

$$0.24\ E\ C$$

if measured in gram-calories. The change in the system is a change of concentration in the "small" cell II; c_1 has decreased and c_2 has increased, because 0.0000026 C gram-molecules KOH have been transported from the anode (c_1) to the cathode (c_2) and at the same time 0.0000052 C gram-molecules H_2O from the cathode (c_2) to the anode (c_1).

In the second step of the cycle they are transported back by means of isothermic distillation, so that the system is brought back to its initial condition. The work corresponding to the transportation of 0.0000026 C gram-molecules KOH from c_2 to c_1[1] is found from equation (11); it is

$$0.0000026\ CRT\left[g_1 \log p_1 - g_2 \log p_2 + \int_{g_1}^{g_2} \log p\ dg\right].$$

The work corresponding to the transportation of 0.0000052 C gram-molecules H_2O from c_1 to c_2 is found from equation (10); it is

$$0.0000052\ CRT \log \frac{p_1}{p_2}.$$

The arithmetical sum of all the amounts of work, performed by the system in this reversible isothermic cycle, must be zero. This gives

$$O = 0.24\ EC + 0.0000026\ CRT$$

$$\left[g_1 \log p_1 - g_2 \log p_2 + 2 \log \frac{p_1}{p_2} + \int_{g_1}^{g_2} \log p\ dg\right]$$

[1] More strictly, from a concentration slightly above c_2 to a concentration slightly below c_1, because in the first step c_1 and c_2 have been changed. But it is simpler, to use c_1 and c_2 directly in the above calculation, as the error due to this simplification can be made negligible by taking C sufficiently small. For C we are justified to choose any value we like; it falls out of the final equation.

If the amounts of work are measured in gram-calories, we have $R = 2$; in the above equation log means Naperian logarithms; we will introduce ordinary logarithms instead; finally we divide the whole equation by C. Then we get the following equation in which log now means ordinary logarithms and which gives the electromotive force in volts.

$$E = 0.00005\ T\left[g_2 \log p_2 - g_1 \log p_1 + 2 \log \frac{p_2}{p_1} - \int_{g_1}^{g_2} \log p\ dg\right].$$

This equation represents the solution of our problem and will be applied to the numerical calculation of a special case. In the following table the vapor-pressure is given as function of the concentration of KOH; the first line (giving the per cent. of KOH by weight, *i. e.*, the weight of KOH in per cent. of the total weight of the solution) and the third line (giving the vapor-pressure over the corresponding concentration of KOH) are copied from Landolt and Boernstein's "Phys.-Chem. Tabellen" (1894), p. 68 (the values of p being calculated by Errera from experiments of Wuellner). The second line (giving g, *i. e.*, the ratio of the number of gram-molecules H_2O to the number of gram-molecules KOH) I have calculated for the application of the above formula. The values p refer to the temperature 20° C., *i. e.*, $T = 293$.

Per cent. KOH	9.09	16.66	23.08	28.57	32.89
g	31.11	15.56	10.37	7.778	6.349
p	16.38	15.25	13.93	12.40	10.75

If we calculate E from the above formula, by means of these values, we get for $g_1 = 6.349$ and $g_2 = 31.11$.

$$E = 0.037 \text{ volt.}$$

This calculation cannot be made with very great exactness, as the experimental data are not sufficient for a very exact numerical determination of the integral in the above equation. Nevertheless the value 0.037 volt will be sufficiently correct to give an idea of the order of magnitude of the drop of the electromotive force due to local concentration changes in the Edison accumulator. 0.037 volt is the amount by which the electromotive force of a cell in which in the pores of the anode the concentration has decreased to 9.09 per cent. and has increased to 32.89 per cent. in the pores of the cathode, is smaller than the electromotive force of the same cell if the concentration of the solution is uniform throughout the cell. It is very probable that in rapid discharges

concentration changes of this or of even greater amount take place; then there will be a drop of voltage due to these concentration changes of the above order of magnitude or more. At the same time there will be a drop of the voltage, due to the other circumstances discussed in § 2, but as explained there, these do not lend themselves to theoretical calculation, without intricate experimental researches.

DISCUSSION.

Mr. W. McA. Johnson: I am very glad to hear Dr. Roeber's paper, because it agrees almost exactly with some theoretical deductions which I made some months ago, and also with some experimental evidence in the case of two copper oxide plates. The voltage of any electrochemical system, for we can use that term where the electrolyte only plays the part of transferring the energy, and does not enter into the reaction similar to the lead cell, where there is a change from a fluid to a solid state—the voltage of such a cell should theoretically be independent of the concentration. The probable success of the Edison battery is due to the fact that Mr. Edison has made his cells very porous, and has it so arranged that the iron is in good electrical contact with the plates, and similarly the nickel oxide is in good contact with the other plates.

We may compare an accumulator to a man's body with bone, muscle and fat. The lead accumulator has a lot of fat, a little muscle or active material, and the bone is in a rickety condition. The bone, the supporting plate, is mechanically so weak that it is apt to buckle in short circuit. The Edison nickel-steel plate, which is much stronger than steel, is also very tough. It has a very large lot of muscle or active material. The fat in the plate is reduced to a comparatively low degree.

Mr. Carl Hering: The arrangement suggested by Dr. Roeber, of connecting the two cells in opposition to each other, would work in practice only provided there is absolutely no current flowing. If he allowed any current to flow, even the small one for a voltmeter, I am afraid the test would not prove anything, because the slightest current would at once change the results, as one cell would be charging while the other is discharging. But in a theo-

retical discussion, the method may be correct because we can then assume that the conditions remain constant. There is another element which enters into these reactions and that is the thermoelectric factor, to which Professor Carhart called our attention yesterday. Perhaps it would explain some of the discrepancies in the Edison accumulator.

Dr. Roeber: I will first answer the last criticism of Mr. Hering. The thermoelectric factor does not enter into my calculation of the Edison cell. If we calculate the electromotive force of a cell from the heat equivalent of the total energy change in the cell, then we have to take into account not only the change of the chemical energy, but also the heat which is to be supplied to the cell or to be taken away from it, in order to keep its temperature constant; the thermoelectric factor enters here; we get the well-known term containing the temperature coefficient of the electromotive force by which the Helmholtz-Gibbs equation is distinguished from the old Thomson rule. It is just for this reason that I have not used this method of calculation for the Edison battery, because the necessary experimental data are missing. I have therefore used the second method of Section 3 of my paper; in this method the electromotive force of the cell is calculated from the change of what Helmholtz calls the free energy of the system, not the total energy; the formula obtained in this way is absolutely exact, without any term of correction being required on account of the thermoelectric factor. That the thermoelectric factor does not enter here into the question at all, can best be seen from the point of view in which I have explained this second method in Section 3 of my paper; I consider an isothermic reversible cycle; the second principle of thermodynamics requires that in this case the sum of all the (positive or negative) amounts of heat supplied to the system from the outside during all the steps of the isothermic cycle must be zero. It follows at once that the sum of all the (positive or negative) amounts of work performed by the system during all steps of the cycle must also be zero. This latter equation I have used, and it is evident that the thermoelectric factor does not enter into my equation at all.

Concerning the other criticism of Mr. Hering, I would say that if I want to apply the principles of thermodynamics, I must allow the system in question to undergo changes; in my case I must

allow the cell to give out current. If I only know exactly all the changes which occur in the system during all steps of the cycle, then I am all right. It is true I must take out of the cell only an infinitely small amount of coulombs, because for the steps of my cycles which represent isothermic discharges, I assume the electromotive force to be constant. I am justified in doing so, because the final energy equation contains the number of coulombs as a constant factor which then drops out; I therefore can choose its value as I please, and I take it infinitely small.

In reply to Mr. Johnson, I would say that the case treated by him is entirely different from the case treated in my paper. Mr. Johnson considers a cell with a copper oxide electrode and a "hydrogen electrode," with KOH as electrolyte; he investigates how the electromotive force of such a cell differs with the concentration of the electrolyte. In the first place, such a cell differs from an Edison battery in so far, as in the Edison cell during discharge the total concentration of the electrolyte is unchanged, while in Mr. Johnson's cell fresh water is formed. Moreover, what Mr. Johnson investigates is: how does the electromotive force depend upon the total concentration; how does it change when an electrolyte of another concentration is used? What I have discussed in my paper is: how does the electromotive force depend upon local concentration changes in the pores of the two electrodes, when the concentration increases at the one electrode, and decreases at the other, while the total concentration is unchanged? The formula arrived at by Mr. Johnson is therefore entirely different from the formula given in my paper. I think the voltage drop of the Edison battery during discharge is the combined result of the different influences, discussed in Section 2 of my paper. I do not think we are justified in assuming that it is wholly due to an increase of internal resistance.

Mr. Johnson: I think that Dr. Roeber is mistaken. It can only be proven by experimental evidence, by discharging an Edison battery and seeing how quickly it recovers, and in what degree it does recover. The point depends on the porosity of the plates.

Dr. Roeber: I fully agree with Mr. Johnson that this question can only be settled by experiment. In my paper I assume that the Edison battery is what it is claimed to be—an oxygen-lift cell. If it is not then my theory does not apply to it.

A paper read at the Inaugural Meeting of the American Electrochemical Society, Philadelphia, April 5, 1902, Dr. N. S. Keith in the Chair.

ELECTROLYSIS BY AN ALTERNATING CURRENT.

By Joseph W. Richards, Ph.D.

When an electric current passes through an electrolyte in one direction it produces electrolysis, and the ionic products of electrolysis are set free at the electrodes. If the current is interrupted, there is observed a back electromotive force, caused by the tendency of these liberated ions to recombine and produce an electric current proportional to the energy of their recombination. If insoluble electrodes are used, and there is thus a chance for a small accumulation of the ions to remain as such, at the electrodes, this back electromotive force will be equal to the electromotive force required for decomposition.

If, using insoluble electrodes, the current is rapidly reversed in direction, the cathions and anions set free at each electrode in rapid alternation recombine as fast as they are successively set free, and if the recombination reaches an efficiency of 100 per cent. we will have no observable electrolytic effect. If, however, the efficiency of recombination is, from any cause, not 100 per cent., we may expect to see at each pole the results of the electrolytic decomposition. Malagoli (*L'Eclairage Électrique*, **45**, 255 (1898)) made experiments of this nature, using an alternating current of 20 periods per second, and stated that the amount of electrolytic products thus obtained is proportional to the coulombs of current passing, and is dependent upon the electrochemical equivalent of the electrolyte.

If the ions, however, are capable of reacting upon the electrolyte, another cause of imperfect recombination, when using alternating current, may operate. If the anion, for instance, is capable of reacting upon the solution to form an insoluble compound, then any such action which happens while the current is passing in one direction will prevent the recombination of that amount of the anion when the current is reversed, for the anion

which has formed the insoluble compound by reacting upon the solution is no longer in condition to recombine with the cathion, and has been removed from the sphere of action and of recombination. Thus, whatever insoluble compound is formed when the current is running one way, remains formed, and we thus have a product continuously formed. An example of such action is offered by a solution of silver chloride dissolved in sodium hyposulphite (sodium thiosulphate), such as is obtained in the wet processes of silver extraction. If such solution is electrolyzed by an alternating current between insoluble terminals, such as carbon or platinum, there is obtained in the solution a brown to black precipitate of silver sulphide which forms at both electrodes. Just what the steps of the electrolytic action are, it is difficult to say. Very probably, the thiosulphate radical, S_2O_3, splits up into SO_3 and S, the former forming sulphuric acid with the water present, while the latter precipitates the silver in solution as sulphide. Whether the S_2O_3 radical comes from the silver salt in the solution or from the sodium salt is not certain, but it probably comes mostly from the latter. On the reversal of the current, any S_2O_3 radicals unused are immediately recombined, while any sulphuric acid formed is at once neutralized by the cathion, but any sulphide of silver formed during the previous cycle remains unattacked and accumulates. In the experiment to be shown, the solution contains silver chloride dissolved in a 10 per cent. solution of sodium hyposulphite; the electrodes are platinum, and the alternating current is obtained by a transformer from the lighting circuit.

If the ions are capable of reacting upon the electrodes, forming insoluble compounds which are insoluble in the other ionic products, then an accumulation of insoluble product may take place on this principle. If, for instance, the anion forms with the anode an insoluble compound, which is unattacked by the cathion, or is insoluble in the products formed at the cathode, then in measure as such compound forms, during the passage of the current in one direction, it removes that much of the anion from the possibility of recombining on the reversal of the current. An example of such action is offered by lead electrodes used in a dilute solution of sodium carbonate (1½ per cent.) containing a small amount of sodium chlorate (Luckow's solution). This solution is used with lead anodes in manufacturing white lead. On pass-

ing the current, the lead carbonate formed at the anode is insoluble in the solution, and is unattacked by the caustic soda formed at the cathode. Consequently, on the reversal of the current, whatever lead carbonate has been formed has taken so much carbonic acid radical, CO_3, out of the sphere of action, and prevented its recombination on the reversal of the current. As a consequence, some lead carbonate forms at both electrodes, which wear away equally. The yield of carbonate is always much less than with direct current of like ampèrage ; the object of these experiments is to show the qualitative possibility of such reactions.

Another example is obtained by using such metallic electrodes in a sodium hyposulphite solution as are capable of giving insoluble sulphides. Cadmium electrodes in a 10 per cent. sodium hyposulphite solution, with alternating current, become covered with a yellow coating of cadmium yellow or cadmium sulphide. The quantitative yield will be too small to yield commercial results, but the fact that such compounds can be formed by the use of an alternating current is interesting from a scientific and theoretical standpoint.

DISCUSSION.

Mr. C. Hering: Why is it assumed that the silver chloride, which is in solution, is not also electrolyzed in this case?

Dr. Richards: It is quite possible that the silver chloride is electrolyzed, and the silver, or a part at least, I suppose must be altered to chloride again.

Mr. Hering: Why can it not be assumed that the silver is dissolved by the thiosulphate just as well as that the thiosulphate is dissolved by the silver chloride?

Professor Richards: It is only a question of the relative quantities. If we had a solution of silver nitrate and put into it $Na_2S_2O_3$ and thus obtained the solution, I would designate it the other way.

Mr. C. J. Reed: After we get them in solution, the current is accessible to both of them.

Dr. Keith: Yes, as far as that is concerned; but the cation is silver and the anion is chlorine. The hyposulphite is not a true electrolyte.

Mr. Reed: How do you find that out? Dr. Richards says the thiosulphate is what decomposes.

Dr. Keith: That is a secondary reaction.

Mr. Reed: How do you prove that?

Mr. Hering: If Dr. Keith can tell us a simple method of finding out exactly what the ions are, many of us would be very glad to hear it.

Dr. Keith: This is only an assumption. I consider it on the principle involved in the electrolytic treatment of lead when we take sulphate of lead, and use as a solvent a solution of acetate of soda. The acetate of soda, itself, may suffer decomposition by the action of an electric current, if it is of too great density; but I assume, and I have no reason to doubt it, except perhaps for some academic reason, that the sulphuric acid radical is one ion and that lead is the other. The sulphuric acid acts to form a sulphate of lead at the anode and lead is deposited at the cathode.

Mr. Reed: I would like to ask Dr. Richards whether, according to the rule he stated for the first case, a plate of lead immersed in sulphuric acid would not form lead sulphate, and would not that lead sulphate continue to scale off and drop to the bottom. Suppose I take a platinum plate and a lead plate in dilute sulphuric acid. The ion liberated at the platinum plate would be hydrogen, which does not dissolve lead sulphate. The substance formed on the lead plate would be lead sulphate; consequently, according to that rule, should there not be a continuous formation of lead sulphate which would continue to scale off and drop to the bottom if you had a platinum and a lead plate immersed in dilute sulphuric acid?

Dr. Richards: I should say that if you took two plates of one kind, one attackable and the other not attackable, you should have the same effect whether you used one plate of lead or both plates of lead; you should have the same effect.

Mr. Reed: But that does not occur with lead plates in sulphuric acid.

Dr. Richards: My recollection is that I tried it with one attackable plate and one lead plate and did obtain it with carbonate solution.

Mr. Reed: Did you obtain it with sulphuric acid?

Dr. Richards: I have not tried the sulphuric acid.

MR. H. RODMAN: If you used the lead plate in solution with sodium carbonate, would you not get the peroxide there?

DR. RICHARDS: It depends upon the current density. By using the proper current density, you get lead carbonate; by using a high current density, you get lead peroxide. With a certain density you will form carbonate of lead—a density of about fifty amperes per square meter.

DR. KEITH: That implies a change in the density, a change in the potential between the plates, and therefore the difference in potential may produce different results in the way of decomposition.

DR. RICHARDS: The difference in current density is connected with the difference in potential and therefore by using a higher potential you get lead peroxide on the plates.

MR. J. C. HECKMAN: In using an alternating current, you get a continuously fluctuating current density, and therefore do you not get a mixture of products?

DR. RICHARDS: You have it fluctuating up to a certain maximum. Therefore, if you keep it within certain limits, you will get a limited product. If you get it up too high, you would, theoretically, get the mixture of peroxide with carbonate.

A MEMBER: I would like to ask you, in that connection, if you used any means of measurement of any kind. If you connected an ampere Siemens dynamometer in series, could you not determine the amount of changes in the character of current?

DR. RICHARDS: I did not use those instruments. My experiments were simply made qualitatively. I took the alternating current with one or two lamps, and placed them in series with the solutions. The solutions I used were these. I have made all those experiments and have gotten the precipitates with all of them. The most successful was usually the one which is at present on, although I used with that silver electrodes instead of platinum electrodes, which are in now, and the precipitation was immediate—inside of a minute. The solution darkened, and we obtained an amount of silver sulphide which was weighable. It was weighed and compared with the number of amperes which we knew were going through, and obtained an efficiency of something between fifteen and twenty per cent. on the current passing; so we knew with absolute certainty that we obtained the

electrolysis, and we obtained the product and weighed it. As I say I do not know whether the failure of these experiments is due, and perhaps it is in this case, to using platinum electrodes instead of silver, or to the character of the current. There is some action on the cadmium electrodes, and while they are in the solution there is a slight yellow tint upon them, but it is not as satisfactory as I would like to see.

Mr. W. McA. Johnson: I think the frequency of the alternations has a great deal to do with it. If you had a frequency that was less you would get considerable electrolysis. If you get that down to a minute or a second or 66/100 of a second, it will make a great deal of difference. It is all between those limits. If you have it instantaneous, of course the forces go right up, and if you have very rapid alternations, like in a Tesla machine, you get very little. If you have an induction coil, you undoubtedly do get an electrolysis, as a person who has measured electrodes by means of the Cotrox bridge finds that if you platinize your electrode you get a very good minimum. If you just use plain platinum, you will not only get a poor minimum, but you will see an evolution of gases, and it is all between those limits, between 100,000 alternations a second, and, we will say, 1. I should say that, not only the current density, but also the number of alternations per second,—that is, the frequency—would be a very strong factor in determining the amount of insoluble product formed.

Prof. C. F. Burgess: We have done a considerable amount of work on the study of alternating current electrolysis, in the electrochemistry laboratory of the University of Wisconsin, and our experience has been that the current density has a very marked effect on the current efficiency. With a low current density, no electrolytic effect is noticeable, or at best you get only a low efficiency, the current efficiency of electrolysis increasing with the increase of current density.

A point which was mentioned a moment ago is worthy of consideration in the study of this subject, namely, the rectifying effect. With certain combinations of electrodes, even with two electrodes of the same material, you may have an asymmetrical conductor. The current thus flowing in one direction more readily than in the other will give a direct electrolytic effect that shows itself by the product at the electrodes.

Much of our work has been done in determining to what extent the alternating current might cause corrosion of water-pipes, this being a matter of practical importance in the proposed substitution of alternating currents for direct currents in power distribution for street railways. We found that under certain conditions we would get appreciable electrolysis, and under other conditions no such effect could be observed. Electrolytic corrosion seemed to be more noticeable where the materials were embedded in sand saturated with the electrolyte than when immersed in a solution. The corrosive effect, however, is very small in comparison with the electrolysis produced by the same amount of direct current. Perhaps 1/1000 would be a large proportion. Alternating current electrolysis does not seem therefore to be of very much practical importance in this question.

Dr. Richards: I fully agree with Professor Burgess as to the small amount and low efficiency of the output. It was merely to call attention to it as a qualitative reaction, that I had in mind. The output certainly decreases with the frequency of the alternations. The slower the alternations, the larger the output; the higher the frequency the greater the reduction of the output. That has been my experience in that line. As I say, I do not know the frequency of this current, or how it compares with the current which I used before; and in this case I have platinum electrodes instead of silver electrodes, but, theoretically, that should not make any difference. This solution, in my previous experiments, turned black and gave a precipitate inside of half a minute. As I said before starting, I could not, under the conditions, guarantee the success of these experiments.

Mr. Reed: It seems to me that all these results are in exact accord with what we ought to expect, theoretically. Any electrochemical reaction is necessarily reversible, provided the products of the electrochemical reaction do not escape and get out of the circuit.

Now, with regard to the alternating current, it is in one direction for a very short time. The product formed at the electrodes cannot escape, no matter whether it is a solution or a solid. The current, reversing so quickly, reverses the electrochemical action, so that it brings it back to its original condition, and therefore we see no change. But it is possible that in most cases, especially

where gases would be formed, some of the products do escape, and I think the products we do get are what escape reversal by getting out of the circuit. That accounts for the very low efficiency. The same thing will account for the fact that with an increased number of alternations the product must necessarily diminish.

Mr. Hering: There is also a true condenser action, as I understand it, in all such cases, and some of the current must necessarily go to charging and discharging the condenser formed by the electrodes.

Mr. Waldo: The frequency being used now is 35. It is considerably lower than that used in the ordinary lighting system.

Dr. Richards: Under those circumstances, I simply must confess that we do not know the conditions which make it act in one case and not in the other.

A paper read at the Inaugural Meeting of the American Electrochemical Society, Philadelphia, April 5, 1902, Mr. Hering in the Chair.

THE ATOM OF ELECTROCHEMISTRY.

By Arvid Reuterdahl, Sc.B., A.M.

An acquaintance with the genesis and evolution of any branch of human knowledge is an extremely valuable aid towards the adequate understanding of its present stage of advancement. We will, therefore, set forth in brief, the evolution of the doctrine of atomism. The universal mutability and changeability of things gave rise, in the early history of thought, to the idea of an abiding ground for all these changes. As the result of this there arose the conception of a cosmic matter or "world-stuff" from which all things originate and into which they become again transformed.

Ancient thought is impregnated with such conceptions. As early as the sixth century, B. C., speculative thought in India concerned itself with these ideas. That brilliant Indian thinker Gautama, commonly known as Buddha, made the following interesting remarks during the course of one of his conversations: "The world is full of changes and transformations. Is there nothing permanent in the world? All compounds will be dissolved again, but the verities which determine all combinations and separations as laws of nature endure forever."

At about this same time we find a number of speculators construing theories about the nature of this world-stuff. Early Greek thought regarded it as self-evident that the cosmic matter must be in itself living and animated. The wonderful mobility and changeability of water and air led Thales to suppose that the world-stuff must be water while Anaximenes declared it to be air.

Anaximander added the attribute of infinity to the idea of primitive or cosmic matter because he argued that a finite world-stuff would soon exhaust itself in the ceaseless succession of productions. He was also convinced that no material and perceptual thing of experience could satisfy the requirements of the con-

cept, primitive matter, and he therefore maintained that cosmic matter had never begun to be, and was imperishable, inexhaustible, and indestructible.

The notion of the indestructibility of matter is, therefore, a very old one.

Parmenides differentiated between the ideas of corporeality or materiality and empty space. For Parmenides, that which "is" means merely that which fills space in contradistinction to that which "is not" or empty space.

The idea of "elements" was put forward by Empedocles who held that out of the mixture of the four elements earth, water, air, and fire arise the individual objects of experience. The four elements were supposed by Empedocles to be homogeneous, imperishable, without beginning and unchangeable. The properties and qualities of individual things were due according to his notion to the kind of mixture and these qualities were often vastly different from the properties of the four original elements.

Anaxagoras developed the doctrine of Empedocles. Instead of the four elements of Empedocles, Anaxagoras substituted the idea of a countless number of elements which differed in color, taste, and form. These numerous elements, he maintained, were present throughout the entire universe in a very finely divided state. By the aggregation of these finely divided elements individual things arose, while by their separation these same things passed away. They were capable of being moved in space but the cause of this motion was not within themselves but resided in a special sort of matter, the lightest and most mobile of all forms and capable both of moving itself and the rest. Anaxagoras called this force-substance *νοῦς* or "thought-stuff."

The world of Anaxagoras was, therefore, the result of the interaction of two forms of existence, the simple elements and the force elements. Although Anaxagoras put a slightly different interpretation upon his *νοῦς* or force-element than the modern physicist puts upon the concept, "energy," nevertheless he practically announced, at this early time, the dictum of modern science which says that there is nothing in the world save matter and energy.

Leucippus, on the basis of the work of Parmenides and Anaxagoras, advanced the idea of atomism. He held that the world consisted of a countless number of imperceptibly small

particles that differed only in form, position and size. To these little particles which Leucippus termed "atoms" (ἄτομοι) were ascribed the power of self motion. Each individual atom was gifted with its own peculiar type and variety of motion. This motion of the atoms was as much without beginning or end as their very existence. All change was due merely to the motion and coming together of the atoms in empty space. The atoms which dart confusedly about in empty space strike together here and there and act upon each other by pressure and impact to form groups or aggregations which, according to mathematical necessity, produce a whirling or vortex motion of the entire complexity which in turn draws into itself adjacent atoms until even entire worlds are formed.

These reflections of Leucippus remind one very much of the nebular hypothesis advanced by Kant in 1755 and afterwards by Laplace in 1796.

Assuming the validity of the main postulates of Leucippus, Democritus declared that inertia or degree of mechanical movability, density and hardness were properties of things. From the two fundamental concepts of matter and motion Democritus built up the world.

After the time of Democritus very little if any advance was made in the theory of atomism until in the sixteenth century, A. D., when the Italian natural philosopher, Giordano Bruno, connected his conception of the "monad" with that of the "atom" of Leucippus.

It remained for Leibniz, the inventor of the infinitesimal calculus and the originator of the conception of *vis viva*, to perfect the notion of a force substance in his Monadology. The monad of Leibniz is essentially a center of force. He sought the ground of motion of bodies not in their extension and mass, but in their ability to do work. The essential nature of bodies is, therefore, force and their property of filling space and being in motion is due to this force.

The Italian mathematician, Boscovich, did considerable to propagate the conception of a center of force atom.

In more recent times we find Ampere, Faraday and Fechner advocating this same theory.

The modern atomic theory is a correllate and consequence of the development of the "Kinetic Theory of Gases." This theory

was advanced and elaborated chiefly by such men as Kroenig, Clausius, Maxwell, Boltzmann, Stefan, Pfaundler, Boyle and Mariotte, Charles, Dalton, Avogadro and Gay-Lussac.

This much-talked-of theory maintains that a gas is composed of a great number of exceedingly small and solid particles which may be either in the atomic or molecular form. These particles are in continuous motion in a straight line. None of this motion of the gaseous particles is lost or destroyed but it is all conserved because of their absolute elasticity. Although the rectilinear motion of a gaseous particle, therefore, is continuous forever, nevertheless the direction of this motion is changed on account of collisions which occur among the particles. Mutual action between the particles does not occur except within very small distances and during extremely small periods of time. Hence the duration of the free and rectilinear motion of a particle is infinitely great as compared with the duration of mutual action and of the time of collision.

The experimental investigation of the properties of gases brought forward the significant fact that when gases react they do so in accordance with definite mathematical laws which indicate that the ultimate gaseous particles are constant quantities as far as their mass is concerned, and that they combine chemically in such volumes as bear simple ratios to each other.

This is practically Gay-Lussac's law which states that when different gases unite chemically the volumes of the reacting gases, measured under similar conditions, bear simple ratios to each other, and the volume of the resulting compound, if gaseous, also stands in a simple ratio to the volumes of its compounds.

It was, for instance, determined by experiment that when hydrogen gas and chlorine gas combine they do so in the proportions of two volumes of hydrogen and two volumes of chlorine. The gas resulting has a bulk of four volumes.

Furthermore, the combining volumes of hydrogen gas and chlorine gas have the mass ratio of 2 : 70.74 or 1 : 35.37. Now, Lothar Meyer and Seubert give the atomic weights of hydrogen and chlorine as 1 and 35.37, respectively.

As the two gases, hydrogen and chlorine, will always combine according to this mass ratio, no matter what arbitrary mass is chosen for either gas, the modern school of chemistry drew the conclusion that the ultimate units or "elements" of matter, as

they called them, must possess a determinate and fixed nature. The elementary atom must, therefore, have a constant and indivisible mass, since if this were not so, there would be no apparent reason remaining to explain the fact that all chemical combinations take place according to definite and unchangeable mass ratios.

The doctrine of the infinite divisibility of matter which had been maintained by many since the time of Zeno as a corollary to that of the infinite divisibility of space was thus held to have been completely overthrown in view of the undeniable evidence of experimental facts. Bodies can be separated into molecules which, in turn, can be divided into atoms, but the atoms of the modern chemist cannot be subdivided. The atom of modern chemistry is thus the limit of actual divisibility of matter.

The advent of this chemical theory of atomism was hailed with universal enthusiasm because it apparently savored so much of the essence of fact.

By means of these modern scientific discoveries it was thought that the notion of the atom had been cleansed from all germs of fantastic speculation and had been brought into the realm of the actual and computable.

The application of mathematical analysis to physical phenomena has enabled the modern physicist to calculate the diameter of a molecule upon the assumption of the validity of certain laws of thermodynamics. Assuming with van der Waals the validity of the equation of state of an ideal gas, $pv = R\theta$, where p is the pressure, v, the volume, θ, the temperature, and R, a constant quantity. We can write this equation in the form

$$(p + a/v^2)(v - b) = R\theta,$$

which equation can, according to Clausius, be presented in a slightly altered form,

$$\left(p + \frac{a}{\theta(v+\beta)^2}\right)(v - b) = R\theta.$$

From this equation an expression for the molecular diameter can be obtained.

If L represents the mean free path of a gas molecule, *i. e.*, the average distance traversed before a collision, N the number of molecules per unit of mass and σ the molecular diameter, we can obtain by substituting the value

$$N = \frac{1}{\sqrt{2}\pi\sigma^2 L}$$

in the equation

$$b = \frac{N 4\sqrt{2}\pi\sigma^3}{\sigma},$$

an expression,

$$\sigma = \frac{3}{2} b\ L\ ,$$

from which the molecular diameter can be computed.

Using this value of σ for carbon dioxide (CO_2) its molecular diameter can be calculated to be 2×10^{-8} centimeters. In other words, about five millions of carbon dioxide gas molecules placed in a row would occupy one millimeter.

The molecular diameters of a number of substances have been obtained in a similar manner by van der Waals and Loschmidt.

Although this atomic theory seemed to be substantiated by fact, yet certain difficulties arose when the attempt was made to explain the phenomena of the transmission of a disturbance from one point to another in empty space. A demand was then felt for a medium of transmission for such disturbances. If a steel rod is caused to vibrate at one of its ends the other end will also experience some disturbance. This simple fact was comprehended with ease, because there existed between the two ends the medium of the rod itself, within which the disturbance could be transmitted. But it was not so easy to explain how a disturbance at one end of the rod could be transmitted to the other end if there existed an opening or crevice through the entire rod at some point between the two ends.

Similar considerations gave rise to a new theory of vortex atoms in a homogeneous, incompressible, and frictionless fluid which served as the medium for transmission of all types of disturbances.

Up to this stage, matter had been regarded as discrete; now the idea of a continuous matter was preferably substituted.

Lagrange laid the foundations for a mathematical theory of fluid motion.

Beginning with the fundamental equations known as Euler's Equations of Motion which pertain to the motion of ideal fluids which are assumed to be incompressible, the so-called "equation of continuity"

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} = 0$$

can be established if the density ρ of the fluid is regarded as constant.

Helmholtz ingeniously investigated this equation and formulated the results thereof in the following theorem: No rotation can be set up in an ideal fluid if the forces have a potential. In this case the particles which rotate already, continue to rotate, but the particles which do not rotate from the beginning will never rotate.

This theorem of Helmholtz led Lord Kelvin to formulate a theory of vortex atoms which are primarily spinning elements of fluid in a fluid. Kelvin's atom is, therefore, a vortex ring of ether spinning in the ether.

In regard to this vortex atom of Kelvin, that eminent authority Maxwell says: "The vortex ring of Helmholtz, imagined as the true form of the atom by Thomson, satisfies more of the conditions than any atom hitherto imagined. In the first place, it is quantitatively permanent, as regards its volume and its strength, —two independent quantities. It is also qualitatively permanent as regards its degree of implication, whether 'knottedness' on itself or 'linkedness' with other vortex rings. At the same time, it is capable of infinite changes of form, and may execute vibrations of different periods, as we know that molecules do. And the number of essentially different implications of vortex rings may be great without supposing the degree of implication of any of them very high."

The attempt will now be made to test the various theories set forth in order to determine to what extent they are consistent with themselves and with facts.

The implications of the kinetic theory of gases will be discussed first.

The fundamental assertions of this theory may be analyzed into three primary hypotheses:

First. A gas consists of extremely small and indestructible portions of matter whose volume and mass are constant.

Second. The particles which compose a gas possess absolute elasticity.

Third. The gas particles are free to move perpetually in rectilinear directions because they do not exert any mutual effects upon each other except at extremely small distances.

The first hypothesis is held to be true by the evidence of experiment. When a portion of matter is subjected to chemical and mechanical action experience invariably shows that no loss of matter occurs with these operations. The balance when used as a comparator of masses, it is claimed, asserts the constancy of mass. The reason for this indestructibility of mass is then found, by the modern atomist, in the constancy of the atomic mass. Yet weight is nothing but the force of attraction between masses. The magnitude of a mass is therefore measured in terms of force. Hence constancy of mass reduces to nothing more nor less than the continuance of force. It is evident that the atomic hypothesis in no way explains this unceasing activity of force.

The modern atomist in order to account for the indestructibility of mass must, therefore, explain the continuance of force. By postulating this continuance of force as a property of the ultimate atom you do not explain it nor do you explain its actual occurrence in observable masses.

The first arbitrary assumption of the kinetic theory is, therefore, incapable of explaining the observed facts of experience.

The second hypothesis is practically implied in the first, because the absolute elasticity, in its ultimate analysis means simply that the particle will react in a definite manner against any force which tends to produce any change in its volume. In a case of a perfectly elastic body the resisting force will be strictly proportionate to the applied force which tends to produce the change in the volume and form of the body. This is precisely the case of an ideal gas as the force with which it resists compression is proportional to the applied compressing force.

The second hypothesis does nothing more nor less than postulate the observed elasticity of a measurable quantity of gas within the gas atom and then maintain that this is all that is necessary to explain the phenomenon. To assign the attribute of elasticity to the atom is merely to incorporate the desired conclusion within the assumption. Every valid hypothesis must correllate into one unit the fact presented for explanation and a fact grounded in experience which explains it.

By violating this fundamental principle of a valid hypothesis, it would manifestly be very easy to deduce any desired conclusion by simply presupposing the necessary elements for this conclusion within the original assumptions.

The third hypothesis seems to entirely ignore all analogies and facts of experience and start out with so improbable and unwarrantable assumptions that one certainly marvels that the kinetic theory has been able to gain so many adherents.

Not in the whole realm of physical phenomena is there a single parallel to the supposed absolute independence of motion and freedom from mutual action which is held to be true of the ultimate particles which constitute a gas.

This by no means ends the matter. To cap the climax, the hypothesis, boldly and in the face of this first assumption, asserts that there is violent mutual action between colliding particles for a very brief period of time before and after impingement. How two such diametrically opposed notions totally unwarranted by experience could have been combined within the same hypothesis is certainly a marvel beyond comprehension.

Not even one of these three fundamental assumptions of the kinetic theory can withstand critical examination. Nevertheless this theory has stood supreme. Certain shortcomings of this theory have been discerned by many eminent physicists and frantic attempts have been made to bolster up the sick theory.

Helmholtz and Kelvin have spent much labor and ingenuity in attempting to save the kinetic theory from oblivion.

Although the vortex atom is unquestionably the product of profound discernment combined with marvelous mathematical sagacity, nevertheless its numerous contradictions prohibit it from ever becoming a sound and fruitful theory.

The ether regarded as a perfect and homogeneous fluid is absolutely incapable of making manifest to the senses any change which is supposed to occur within it.

A hypothetical displacement of, for example, one cubic foot of ether by a second cubic foot could never become a perceptual fact to a sentient being because this particular spatial cubic foot would at all times contain precisely the same amount of ether. From one moment to the other there would be absolutely no means by which to distinguish a difference or change within the ether.

Maxwell has pointed out another difficulty. Referring to Thomson's atomic theory, he says: "In Thomson's theory, therefore, the mass of bodies requires explanation. We have to explain the inertia of what is only a mode of motion, and inertia is

a property of matter, not of modes of motion. It is true that a vortex ring at any given instant has a definite momentum and a definite energy, but to show that bodies built up of vortex rings would have such momentum and energy as we know them to have, is, in the present state of the theory, a very difficult task."

In his article on the "Ether," this same authority says: "No theory of the constitution of the ether has yet been invented which will account for such a system of molecular vortices being maintained for an indefinite time without their energy being gradually dissipated into that irregular agitation of the medium which, in ordinary medium, is called heat."

To these attempts one readily concedes the merit of ingenuity, but even at the best they are scarcely more than interesting exercises in pure mathematics. It is, indeed, wonderful how much earnest thought is put upon allied vaporous subjects. Thus we find, at the present time, enthusiastic mathematicians glorying in that undignified nonsense which they call non-Euclidean geometry. Such men as Lobatschewsky, Riemann, and even Helmholtz advise us not to be too sure that the sum of the angles of a triangle is equal to two right angles before we have determined the sum by measurement of a large astronomical triangle. They also are very anxious to have us believe that because an algebraic expression of the third degree may represent a geometrical magnitude of three dimensions, therefore, there must be a four-dimensional space to correspond to an algebraic expression of the fourth degree.

As far as I know, no one has yet attempted to discover the genuine atom within this four-dimensional space. Certainly within that space some brilliant mathematician ought to be able to find both a most perfect atom and a storehouse for unlimited amounts of energy.

One phase of this subject still remains to be considered. Up to the present point in the discussion it has been taken for granted that given a material world composed of atoms, effects can be transmitted from one body to another. These effects would come under the broad terms of force and energy. In his work on "Matter and Motion," Maxwell expresses this thought by saying: "We are acquainted with matter only as that which may have energy communicated to it from other matter, and which may in its turn communicate energy to other matter." Referring to

energy he says: "Energy, on the other hand, we know only as that which in all natural phenomena is continually passing from one portion of matter to another."

The question before us now is whether the modern conceptions of the constitution of matter are sufficient to explain how such transmission and transfer of energy from one portion of matter to another is possible.

Generally speaking, the amount of a force is measured by the change of velocity which is imparted to the body acted upon. Motion, then, is a perceptual measure of the action of a force upon a body. There is intimately connected with these notions the question whether forces can produce effects from a distance. In direct opposition to this latter idea is that of common-sense philosophy which holds that the indispensable prerequisite of any physical action is that the bodies be in contact in space.

On surveying the entire ground it becomes evident to us that the entire issue hinges on whether an affection of any sort whatever can be transferred from one thing to another.

A hasty judgment would lead one at once to assert that there are no difficulties whatever in this notion, and that it is self-evident that an influence can be transmitted from one thing to another. The general idea regards this influence as proceeding from one body which is active to another body which is passive and to which the influence attaches itself.

In direct opposition to this universal notion we will attempt to establish and maintain the following thesis:

It is absolutely impossible for an *Influence* I whether it be a thing, action, state or force, to be transferred from one thing M to another thing N.

Let us, in the first place, suppose for sake of argument, that the influence I is a thing. The facts of the case then would be that an actually real thing I separates itself from M and then passes over and connects itself with N. This connection which I makes with N may be of the same or of a different nature than that which previously existed between I and M. For illustration, let us take the common case of a moist body M which becomes dry when in the presence of a dry body N which in turn becomes moist. This commonly occurring phenomenon would be explained ordinarily by saying that the changes are caused by the transfer of water I from M to N. If the moist state means simply the

presence of water then neither *M* nor *N* have undergone any real change in nature. Yet it was our desire to show how an influence *I* passing from *M* to *N* could cause a real change in *N's* nature. Nevertheless, *M* and *N* do undergo changes which are genuine changes of nature. As *N* begins to get moist, its constituent particles are forced apart and consequently a larger volume is occupied and a tougher connection is formed between the particles. Similarly the drying body *M* shrinks and becomes more brittle. What is therefore desired, is to understand how the presence of water *I* in the body *N* causes the real changes in *N's* nature. It remains, therefore, to explain how *I* can effect *N*, and we are hence no nearer the solution of the problem how *M* can affect *N*. In order to obviate this difficulty the suggestion will undoubtedly be made that this affection *I* is not a thing but is an action, state or force. Thus, it is thought that the necessity of explaining how the transferred thing *I* acts upon the thing *M* is entirely avoided. Nevertheless this launches us into the new difficulty of explaining how a state *I* can separate itself from a body *M* and exist for even an infinitely small portion of time between *M* and *N* as the state of neither. This same difficulty would pertain even if the contention were made that it is an action or force which detaches itself from *M* and attaches itself to *N*.

Even if it were admitted that an action, state or force, *I*, could detach itself from *M*, what is to fix its direction towards a body *N* in preference to any other direction towards a body *O*? To suppose that body *M* has given to *I*, its direction forces us again to demand an explanation of how action takes place between *M* and *I*. There is evidently no reason why *M* should so decidedly favor *N* more than *O* or *P* or any other body. Consequently there remains nothing to assume but that at the time of transition, *M* must be subject to some counteraction of *N* only and not of *O* which restricts the influence *I* to move to *N*. This would be to again presuppose the very action between *M* and *N* which we have been trying so ardently to explain. Furthermore, there is no reason why this now independent and free action or state *I* should not continue its excursion through the universe forever without attaching itself to either *N* or *O* or any other body whatever. The further assumption must, therefore, be made that *N* has some kind of a selective power by which it checks the further and otherwise indefinite motion of *I*. Still another implication

is involved which calls for an explanation and that is how a free action or state *I* not belonging to any particular body should unite itself with an equally free and independent body *N* to become its state and, therefore, to cause a genuine change in *N*.

The resort to the notion of contact in space by no means helps the situation. If it were granted outright that all action between bodies is and must inevitably be preceded by contact in space, there would still remain the necessity of explaining the law which governs the fact that spacial contact is the indispensable condition which must be satisfied before mutual action between bodies can take place. Certainly the mere conception of spacial contact does not involve as a self-evident fact the idea of mutual action. The familiar instance of motion apparently produced by mere impact of bodies will undoubtedly be pointed to as a strong argument in favor of the value of spacial contact as a means of producing mutual action. In diametric opposition to this, we will strongly urge that motion can only be an effect of forces which act at a distance and those portions of bodies which are in genuine contact are absolutely worthless so far as the production of motion is concerned. By genuine contact it must be understood that the boundaries of the two bodies are either common, as in a point without extension or coincident as in a surface without thickness. Manifestly it is only those portions of the bodies which do not occupy the same space which can be at all conducive towards the production of motion. Those parts which do occupy the same space and which are, therefore, in genuine contact can certainly not be productive of motion.

This conclusion cannot be avoided by supposing that a moving body *M* communicates motion to a body *N* which is at rest. This would bring us back to our previous reflections in regard to the transmission of an influence *I* from a body *M* to a body *N*. That such a transmission is impossible has already been clearly shown. Furthermore, motion can hardly be honored with the dignity of being called a state as it is merely an occurrence or change which the moving body undergoes.

The previous discussion converges into the inevitable conclusion that affinity or action between distant elements must be admitted.

The critical examination of atomism has brought out so many implications and contradictions in the two conceptions, the cor-

puscular and the ether atom, that there is practically no alternative left except the unextended atom or center of activity.

This latter we will now discuss in brief. The primary supposition which must be made concerning a real atom is that it is essentially a unit. Anything which contains parts which are subject to distinct experiences not felt alike by all the parts cannot presume to be a genuine unity. A real unity X must be so constituted in its nature that an impression or effect made upon the point x' must be at once an effect or state of the whole of X. If the state must first be transmitted from x' to y' and so on to all the points of X before it can be a state of the whole of X, then we may as well substitute a corresponding number of separate and distinct parts, because this is just what is supposed to happen in the case of separate elements. Such a unity would be entirely without value and significance since any collection of distinct and separate elements would require the same procedure. A real and unitary atom must, therefore, be such that a state experienced at one of its points, x', must be felt with equal intensity in the whole atom without requiring any process of transmission from this point to any other. Hence, every motion imparted to the point x' of the atom X must, therefore, be a genuine motion of a diametrically opposite point y'. This means that it must take absolutely no time to communicate the motion from point x' to point y' along the line $x'y'$. Furthermore, the point y' must experience as strong an effect as the point x'. Nevertheless, actual and undeniable experience teaches us that there is a variation of the intensity of a force with the distance. If we are to maintain both the unity and the extension of the atom, we violate facts of experience. We certainly cannot give up the unity of the atom and, therefore, we must give up its extension.

We have now reduced the world to a system of centers of activity which effect each other at a distance. There remains for us, however, to account for the fact that one element is able to effect another at all. We have already been obliged to part forever with the idea that an influence can be transmitted from one element to another. The only way to solve this problem is by giving up the independence of the elements which constitute the world.

We will endeavor to point out in brief a line of thought which satisfactorily meets these perplexing questions.

Let us represent the sum total of the really existent by S. Then we can represent S as a function of the individual elements u, v, w, etc., into which this totality seems to be differentiated. All the other remaining elements besides u, v, and w which particularly attract our attention may be represented by R. Using these symbols we can formulate the expression

$$S = f(u, v, w \ldots\ldots\ldots\ldots R).$$

In order to illustrate the application and interpretation of this formula, we will suppose that a change in the element u has taken place so that it has become u'. Unless some compensating change takes place in the expression

$$f(u, v, w \ldots\ldots\ldots\ldots R),$$

we will no longer be able to equate it with the expression S.

To reestablish the equality of these two expressions, one or more of the remaining elements of S must sustain a change of state. Hence, we may assume that a change of v's state to v' is, in this case, all that is necessary to equalize the change of u to u'. The expression for S is sufficiently broad and flexible to allow an infinity of possibilities. Thus, we may assume that if a change of state were to occur in w so that this element becomes w' then a change in only one element will not be sufficient to restore the equality, but a change of all the remaining R elements to R' will be necessary.

It is evident that our function S is capable of innumerable combinations and permutations; hence, no further attempts will be made to illustrate these possibilities.

There is one thought, however, which should be emphasized and that is that the various elements u, v, and w are not independent, and consequently do not require either the transmission of some influence from one element to another or the presence of some medium within which to transmit it. On the contrary, the elements are absolutely dependent and related to each other in accordance with some rational ground. Every change in any single element is known immediately to the entire function S and the requisite compensating changes, whatever they may be, will take place without the necessity of the transmission of hypothetical effects from one element to another. By means of this conception it is evident that the notion of action at a distance loses all its terrors and becomes perfectly clear and explicable.

The scope of this paper does not allow us to make detailed applications of the principles set forth to that infant science, electrochemistry. The atom of electrochemistry can in no way differ from the atom of science in general, hence, what has already been said about the atom must be true of it in this field also. Such a brilliant investigator as Faraday keenly appreciated the entire usefulness of the corpuscular and extended atom. Tyndall clearly states Faraday's views concerning this subject as follows: "What do we know of the atom apart from its force? You imagine a nucleus which may be called *a*, and surround it by forces which may be called *m*; to my mind the *a* or nucleus vanishes and the substance consists of the powers *m*. And, indeed, what notion can we form of the nucleus independent of its powers? What thought remains on which to hang the imagination of an *a* independent of the acknowledged forces? These thoughts of Faraday are evidently in complete agreement with our own line of reasoning. It is, however, extremely doubtful that the so-called atom of both chemistry proper and electrochemistry is an ultimate atom. It is vastly more probable that this so-called atom consists of a number of ultimate atoms acting as one stable group. The researches of Faraday were potent in bringing forward the conception of the "ion" or charged atom or group of atoms. Furthermore, he showed conclusively that all atoms possess either equal capacities for electricity or simple multiples of the capacity of the univalent atoms.

In conclusion I would suggest that it is along the avenue of electrochemistry that we may expect radical advancement in the science of electricity. By studying the activities of atoms under the favorable conditions of dissociation, facts will undoubtedly be discovered which will render the varied phenomena of electricity more intelligible. As a result of this work I predict that the absolute correllation and identification of the phenomena of electrostatics, electrodynamics, and electrolytics will ensue.

Setting out with the fundamental supposition that an ion is a center or group of force centers, I arrived at the conclusion that ionic conditions must exist in the realm of both electrostatics and electrodynamics. As a result of these reflections I became convinced of the truth and validity of the following theses:

1. The laws and facts of dissociation can, in general, be applied to both static and dynamic electricity.

2. The conductivity of all substances is due to the presence of ions.

3. The "specific resistance" of all substances is intimately related to the state of ionization.

4. The phenomena of magnetization is due to the existence of ionic conditions.

The recent work of J. J. Thomson, construed in the light of these assertions, can plainly be used as evidence in corroboration of their validity. J. J. Thomson has shown that there is a definite connection between the dielectric constants of solvents and their dissociating power. Expanding upon this observation we may say, in general, that the presence of a dielectric is conducive to the production of ions.

It will be impossible within the limits of this paper to discuss this matter at any greater length. Suffice it to say, in closing, that the manifold phenomena of electricity must ultimately be the result of the activities of the atom of electrochemistry.

OBITUARY.

CHARLES T. CHILD.

Charles Tripler Child, a charter member of this Society, died at Gleasondale, Mass., of typhoid fever, on June 29, 1902. He was born in Richmond, Va., Nov. 1, 1867. He was educated by a private tutor until he entered Richmond College in 1880, leaving five years later and entering the Johns Hopkins University in Baltimore as a special graduate student in physics and mathematics. Soon after leaving the University he was actively engaged in electric railway work, and later in building dynamos, motors, etc. For some time after this he was at the Astro-Physical Observatory of the Smithsonian Institute, in Washington. He also practiced as consulting engineer and took out a number of patents. During the last five years of his life he was editor of various technical journals, first of *The Electrical World*, later of *The Engineering Magazine*, and at the time of his death he was the technical editor of the *Electrical Review*. He was a most popular and highly esteemed member of the electrical fraternity and had many friends. He received the honorary degree of B.Sc. from Richmond College in 1893. He was a member of the American Institute of Electrical Engineers and several other technical societies. On Nov. 30, 1890, he married Miss Bertha Cushing. His wife, daughter, and twin sons survive him.

INDEX.

SUBJECTS AND AUTHORS.

Page.

Accumulator, Theory of the Edison; Roeber 195
Acker, C. E., Paper, 165; Discussion 173
Alkalies and Chlorine; Acker 165
Alternating Current, Electrolysis by an ; Richards 221
Atom of Electrochemistry; Reuterdahl 229
Bancroft, W. D., Paper, 65; Discussions 47, 48, 49, 68, 81, 110, 125
Bisulphide of Carbon in Electric Furnace; Taylor 115
Blackmore, H. S., Discussions 79, 173
Browne, D. H., Discussion 61
Burgess, C. F., Paper, 147; Discussions 48, 162, 163, 226
Carbon, Manufacture of Bisulphide of—in Electric Furnace; Taylor 115
Carhart, H. S., Paper, 105; Discussions .....
..... 47, 48, 109, 110, 113, 117, 125, 127, 138, 162
Carveth, H. R., Discussion 193
Catalogue of Charter Members, Alphabetical, 19 ; Geographical 30
Caustic Alkalies and Chlorine by the Dry Electrolytic Process; Acker .. 165
Child, Charles T., Obituary Notice 246
Chlorine, Alkalies and ; Acker 165
Collins, C. L., Paper, 53; Discussions 60, 61, 62
Composite Metals, Electrolytic Refining of; Ulke 95
Constitution 13
Continuous Electrolysis of Solutions of Metals; Keith 131
Copper Oxide Plate; Johnson 187
Current Electrochemical Theories; Kahlenberg 119
Doremus, C. A., Discussions 46, 50, 80, 83
Dow, H. H., Paper, 127; Discussions 67, 127, 128, 129
Edison Accumulator, Theory of; Roeber 195
Electrical Reduction of Lead; Salom 87
Electrochemical Theories; Kahlenberg 119
Electrochemistry, A University Course in; Richards 41
Electrodes, Graphite; Collins 53

Electrolysis by an Alternating Current; Richards 221
Electrolysis of Solutions of Metals; Keith 131
Electrolytic Production of Zinc from Its Ores; Sadtler 141
Electrolytic Rectifier; Burgess and Hambuechen 147
Electrolytic Refining of Composite Metal; Ulke 95
Geographical Distribution of Members 30
Gladstone-Tribe Couple; Bancroft 65
Graphite Electrodes in Metallurgical Processes; Collins 53
Hambuechen, C., Paper 147
Heckman, J. C., Discussion 225
Hering, C., Discussions .....
62, 91, 109, 110, 127, 129, 138, 144, 145, 146, 162, 173, 193, 218, 223, 224, 228
Historical Sketch 3
Hopkins, N. M., Discussion 61
Howard, H., Discussion 60
Introductory Remarks; Richards 1
Isakovics, A. von, Discussion 173
Johnson, W. McA., Paper, 187; Discussions 67, 89, 193, 218, 220, 226
Kahlenberg, L., Paper 119
Keith, N. S., Paper, 131; Discussions ... 61, 62, 81, 90, 138, 144, 223, 224, 225
Lead, Electrical Reduction of; Salom 87
List of Members, Alphabetical 19
List of Members, Geographical 30
Manufacture of Bisulphide of Carbon in Electric Furnace; Taylor 115
Meeting, Directors 11
Meeting, Executive Committee 12
Meeting, Organization 7
Meeting, Preliminary 4
Metals, Continuous Electrolysis of Solutions of; Keith 131
Meter; Norden 181
Method of Electrolytic Production of Zinc from its Ores; Sadtler 141
Nascent State; Reed 69
New Type of Electrolytic Meter; Norden 181
Norden, K., Paper, 181; Discussion 185
Note on the Gladstone-Tribe Couple; Bancroft 65
Novel Concentration Cell; Carhart 105
Obituary Notice of Charles T. Child 246
Portrait, President J. W. Richards ..... Frontispiece
Rectifier, Electrolytic; Burgess and Hambuechen 147
Reduction of Lead; Salom 87
Reed, C. J., Paper, 69; Discussions .....
..... 83, 90, 92, 109, 110, 128, 138, 181, 223, 224, 227
Refining of Composite Metals; Ulke 95
Relative Velocities of the Ions in Solutions of Silver Nitrate in Pyridine and Acetonitrile; Schlundt 177
Report of Committee on Papers and Meetings 11
Report of Membership Committee 10
Reuterdahl, A., Paper 229

Reversible Copper Oxide Plate; Johnson 187
Richards, J. W., Introductory Remarks, 1; Papers, 41, 221; Discussions 50, 82, 86, 89, 91, 93, 110, 117, 124, 146, 163, 193, 223, 224, 225, 227, 228
Richards, J. W., Portrait ..... Frontispiece
Rodman, H., Discussions 128, 225
Roeber, E. F., Paper, 195; Discussions 109, 110, 219, 220
Sadtler, S. S., Paper, 141; Discussions 144, 145, 146
Salom, P. G., Paper, 87; Discussions 89, 90, 91, 92, 145
Schlundt, H., Paper 177
Smith, A. W., Discussion 47
Sperry, E. A., Discussions 92, 129, 162
Storage Battery, Zinc-Bromide; Dow 127
Taylor, E. R., Paper, 115; Discussion 117
Theories, Current Electrochemical; Kahlenberg 119
Theory of the Edison Accumulator; Roeber 195
Thermodynamical Note on the Theory of the Edison Accumulator; Roeber 195
Townsend, C. P., Discussion 67
Ulke, T., Paper, 95; Discussion 138
University Course in Electrochemistry; Richards 41
Velocity of Ions; Schlundt 177
Waldo, Discussion 228
Weightman, A. T., Discussions 67, 68, 138
Zinc-Bromide Storage Battery; Dow 127
Zinc from its Ores; Sadtler 141

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